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P. 63 line 17, for "sodium sulphate" read "sodium sulphide."

P. 80 line 26 in the table, for "Iodine value of solid fatty acids 101.5" read "10-15."

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CAMBRIDGE

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

AN Ordinary Meeting of the Society was held in the Chemical Society's Rooms, Burlington House, on Wednesday, December 5th, the President, Mr. Edward Hinks, being in the chair.

Certificates were read for the first time in favour of William Bennett Adam, M.A., A.I.C., Alfred Louis Bacharach, B.A., F.I.C., Andrew Dargie, B.Sc., A.I.C., Wadie J. Itayim.

Certificates were read for the second time in favour of Edwin Herbert Bunce, A.I.C., Frederick O'Brien, M.Sc., F.I.C., William Macro Seaber, B.Sc., F.I.C., John Graham Sherratt, B.Sc., F.I.C.

The following were elected Members of the Society:—Charles Wesley Bayley, Harry Brindle, B.Sc., A.I.C., William George Burgess, George Leonard Clothier, Hector Ingram Downes, M.Sc., A.I.C., Alec Walter Greenhill, M.Sc., A.R.C.Sc., A.I.C., Donald R. Hayward, B.Sc., B. L. Khuller, M.Sc., A.I.C., James Donald Kidd, B.A., M.Sc., A.I.C., Herbert Drake Law, D.Sc., F.I.C., Sidney John Saint, B.Sc., A.I.C.

The following papers were read and discussed:—"The Natural Occurrence of Boron Compounds in Fruits and Vegetable Products," by A. Scott Dodd, B.Sc., F.I.C.; "Chemical Tests for Drunkenness: The Determination of Small Quantities of Alcohol in Urine," by John Evans, F.I.C., and A. O. Jones, M.A., F.I.C.; "The Analysis of Mixtures containing Acetone, Ethyl Alcohol and Isopropyl Alcohol," by C. A. Adams, B.Sc., F.I.C., and J. R. Nicholls, B.Sc., F.I.C.; "The Specific Gravities and Immersion Refractometer Readings of Dilute Mixtures of Acetone and Water," by J. R. Nicholls, B.Sc., F.I.C.; and "The Wijs Method as the Standard for Iodine Absorption," by J. J. A. Wijs, Ph.D.

Death.

We deeply regret to have to record the death of Mr. J. H. B. Jenkins, on December 11th, 1928.

The Analysis of Mixtures containing Acetone, Ethyl Alcohol, and Isopropyl Alcohol.

BY CHARLES AMBROSE ADAMS, B.Sc., A.I.C., AND JOHN RALPH NICHOLLS, B.Sc., F.I.C.

(Read at the Meeting, December 5, 1928.)

I. INTRODUCTION.—Both acetone and isopropyl alcohol find application as substitutes for ethyl alcohol, and the analysis of a mixture of the three substances is occasionally required. The object of this paper is to give analytical methods which have proved satisfactory in this laboratory for the past three or four years.

PRELIMINARY REMARKS ON THE DETERMINATION OF ETHYL ALCOHOL.—The usual method for the determination of ethyl alcohol is based upon the specific gravity of its aqueous solution. Many substances, which by their presence would invalidate this method of determination, can be removed by a petroleum spirit and brine separation (Thorpe and Holmes, *J. Chem. Soc.*, 1903, **83**, 314–7). Other substances commonly associated with ethyl alcohol in mixtures may, however, be only partly, if at all, removed by this preliminary treatment, and in this category appear acetone, methyl ethyl ketone, methyl alcohol, isopropyl alcohol, *n*-propyl alcohol, benzyl alcohol, etc. Hence the specific gravity of an aqueous solution of ethyl alcohol containing one or more of these ingredients affords no reliable criterion of the proportion of ethyl alcohol, and the presence of an interfering substance may not be anticipated. The purity of such aqueous alcohol solutions may be tested readily by means of the refractometer, the reading obtained for the test solution being compared with that given by a pure ethyl alcohol solution of the same specific gravity. Tables showing the readings given by the Immersion Refractometer for aqueous solutions of methyl, ethyl, isopropyl and *n*-propyl alcohols obtained in this laboratory by J. Holmes in 1911 have been published (see "Alcohol," by Simmonds; Macmillan & Co., 1919, pages 285 and 287). A similar table for acetone is given in the following paper. A comparative table interpolated from these results is given later in a form convenient for practical use. With the exception of methyl alcohol, solutions of the other substances referred to give higher refractions than solutions of ethyl alcohol of the same specific gravity. Methyl alcohol can be tested for by the Denigès method (Simmonds, *ANALYST*, 1912, **37**, 16; Jones, *id.*, 1915, **40**, 221, etc.). It is to be noted that *n*-propyl, amyl and benzyl alcohols, when present in sufficient proportions, give positive results in this test, which is not, therefore, specific for methyl alcohol. The test is very valuable, however, for indicating the absence of methyl alcohol.

Only in those cases, therefore, where the refractometer reading of a solution, purified if necessary by the Thorpe and Holmes method, agrees with that given by a corresponding solution of ethyl alcohol, and where the Denigès test has given a

negative result, can the specific gravity of a solution be used with certainty for determining the ethyl alcohol.

In our opinion, the refractometer reading (or the determination of some other physical constant) should always be employed as a check upon a determination of ethyl alcohol made from the specific gravity of an aqueous solution, unless the absence of interfering substances is known with certainty.

SPECIFIC GRAVITIES AND REFRACTIONS OF AQUEOUS MIXTURES OF ACETONE AND THE LOWER ALCOHOLS.—In the case of an aqueous solution of acetone or of one of the lower alcohols neither the specific gravity nor the refraction is a linear function of the quantity in solution. When, however, the proportion present does not exceed about 10 per cent. by volume the function is very nearly linear. For purposes of calculation it is convenient to express the strengths of solutions in terms of a common unit, and for this purpose each liquid is regarded as though it were the "proof spirit" of the Official Specific Gravity Tables (H.M. Stationery Office, 1916). The following table shows the relation between percentages of apparent "proof spirit" and percentages by volume of some of the lower alcohols and of acetone. The ethyl alcohol figures are taken from the Official Specific Gravity Tables; the figures for methyl, *n*-propyl and isopropyl alcohols are interpolated from data obtained by Holmes, and those for acetone are interpolated from data obtained by one of us and given in the following paper :

TABLE I.
COMPARATIVE STRENGTHS (PERCENTAGE BY VOLUME).

Apparent proof spirit. Per Cent.	Methyl alcohol. Per Cent.	Ethyl alcohol. Per Cent.	<i>n</i> -Propyl alcohol. Per Cent.	Isopropyl alcohol. Per Cent.	Acetone. Per Cent.
1	0.60	0.57	0.62	0.60	0.76
2	1.20	1.15	1.26	1.20	1.53
3	1.81	1.72	1.90	1.80	2.32
4	2.42	2.29	2.53	2.40	3.11
5	3.01	2.86	3.17	3.00	3.89
6	3.61	3.43	3.84	3.60	4.66
7	4.19	4.01	4.50	4.21	5.41
8	4.76	4.58	5.16	4.83	6.15
9	5.31	5.17	5.80	5.44	6.91
10	5.85	5.73	6.50	6.08	7.69
11	6.42	6.30	7.19	6.69	8.42
12	6.99	6.87	7.87	7.33	9.20
13	7.57	7.45	8.55	7.97	9.94
14	8.13	8.01	9.20	8.59	10.65
15	8.68	8.58	9.89	9.20	11.36
16	9.33	9.16	10.55	9.83	12.05
17	9.88	9.74	11.22	10.47	12.75
Mean value for 1 per cent. proof spirit	0.585	0.573	0.655	0.612	0.760

The use of this mean value will give a percentage by volume not differing by more than about 0.1 per cent. from the correct value.

The following table gives the corresponding refractometer readings. All except the acetone figures, which are obtained from the following paper, are interpolated from data obtained by Holmes in this Laboratory:

TABLE II.
COMPARATIVE REFRACTOMETER READINGS.

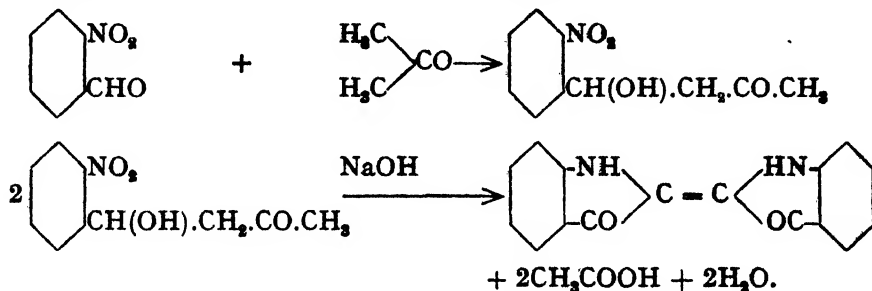
Apparent proof spirit. Per Cent.	Immersion Refractometer reading at 60° F.				
	Methyl alcohol.	Ethyl alcohol.	<i>n</i> -Propyl alcohol.	Isopropyl alcohol.	Acetone.
0	15.4	15.4	15.4	15.4	15.4
1	15.7	16.1	16.5	16.5	16.6
2	16.0	16.8	17.7	17.6	17.9
3	16.2	17.5	18.9	18.6	19.1
4	16.5	18.2	20.1	19.6	20.3
5	16.8	18.9	21.3	20.6	21.6
6	17.1	19.7	22.6	21.7	22.8
7	17.4	20.5	23.9	22.8	24.0
8	17.7	21.2	25.2	23.9	25.3
9	17.9	22.0	26.6	25.0	26.5
10	18.2	22.8	28.0	26.2	27.8
11	18.5	23.6	29.4	27.4	29.0
12	18.8	24.4	30.8	28.7	30.2
13	19.1	25.3	32.2	29.9	31.4
14	19.3	26.1	33.6	31.2	32.6
15	19.6	26.9	35.0	32.4	33.7
16	19.9	27.8	36.4	33.7	34.9
17	20.2	28.7	37.8	34.9	36.0

We have repeatedly found that with aqueous mixtures of these substances, provided the total proportion does not exceed about 10 per cent. by volume, the apparent proof strength and the refraction of the mixture are practically the sum of those due to each of the ingredients. Hence in mixtures of the above substances it may be stated that up to a strength of about 17 per cent. of apparent proof spirit the specific gravities and refractions are, for practical purposes, additive factors. With two known substances alone present the quantities of each can be calculated by proportion from two determinations, *viz.* the specific gravity and the refractometer reading. With three known substances present, if one can be determined by any independent process, allowance can be made for it in the strength and refraction of the solution, and the proportions of the other two can then be calculated. Similarly, in an unknown mixture, any ingredients which can be separately determined can be allowed for, and the resulting figures give a measure of the undetermined ingredients. It is desirable always to have direct methods for the detection and determination of substances likely to be present, and the following methods are applicable to mixtures containing acetone, ethyl alcohol and isopropyl alcohol.

II. THE DETECTION AND COLORIMETRIC DETERMINATION OF ACETONE.—

The test used by Penzoldt for the qualitative detection of acetone (*Deut. Arch. klin. Med.*, 34, 127; referred to in *Z. anal. Chem.*, 1885, 24, 149) appears to have escaped general notice. We have found this test satisfactory for the past four years, and have modified it to furnish a rapid quantitative colorimetric method for the determination of acetone.

When sodium hydroxide is added to a mixture of *o*-nitrobenzaldehyde and acetone, indigo is formed as a condensation product:



The indigo separates almost at once as a flocculent precipitate, and its appearance is conclusive evidence of the presence of acetone. With a very small concentration of acetone, however, precipitation of indigo may not at first be apparent, but the solution will develop a colour ranging from yellow through yellowish-green to greenish-blue, depending on the proportion of acetone present. By allowing the solution to stand for about 1 hour and filtering through a small white paper, a distinct indication of precipitated indigo can be obtained from 10 ml. of a 0.05 per cent. solution of acetone.

The yellow and yellowish-green colours produced in solutions containing not more than 0.2 per cent. of acetone are suitable for quantitative colorimetric determinations. Under the conditions described the colour reaches its maximum in 10 to 15 minutes, and a faint but perceptible colour is given by 1 mgrm. of acetone in 10 ml. (0.01 per cent. of acetone).

The *o*-nitrobenzaldehyde solution used tends to darken in colour on keeping. A recently-prepared solution should be used for quantitative work, and the blank should be colourless. The quantitative method is as follows:—

To an aliquot portion of the distillate to be tested (containing not more than 0.02 grm. acetone and diluted with water to 10 ml.) is added 1 ml. of a 1 per cent. solution of *o*-nitrobenzaldehyde in 50 per cent. ethyl alcohol (not methylated spirit, as this contains acetone). After mixing, 0.5 ml. of a 30 per cent. solution of sodium hydroxide is added, and the test solution allowed to stand for about 15 minutes, avoiding strong daylight. At the end of this time the colour is compared with the colour developed in a set of standard acetone solutions, containing from 0 to 20 mgrms. of acetone in 10 ml., which have been treated similarly at the same time. The range of the colours produced is very marked, and it is possible to have as many as twenty readily differentiated standards within the range suggested.

III. DETECTION AND COLORIMETRIC DETERMINATION OF ISOPROPYL ALCOHOL.

—Isopropyl alcohol can be oxidised readily to acetone, which can then be determined by the above method. We have found the most convenient oxidising agent for this purpose to be potassium dichromate and sulphuric acid under the conditions to be described later.

For the purpose of the routine testing of alcoholic distillates, however, it was desired to avoid the distillation necessary in the dichromate oxidation, and to use a method of oxidation which could be applied simultaneously to a large number of distillates. Various oxidising agents were tried. Dilute nitric acid, hydrogen peroxide and sodium peroxide, tested under various conditions, gave poor results. Potassium permanganate, either in acid or alkaline solution, gave good results, but the use of this reagent necessitated the filtration of the test solutions. Strong nitric acid was too vigorous in its action. Bromine water gave excellent results, and the conditions for the use of this reagent were therefore worked out.

For the detection of isopropyl alcohol in solutions containing ethyl alcohol the method is as follows:—

The test solutions (after appropriate purification) are diluted to a strength of approximately 10 per cent. by vol. of alcohol. To 10 ml. of each solution in a test-tube 5 ml. of saturated bromine water are added. The tubes are lightly corked and allowed to stand for about 3 to 6 hours in the cold, or even over-night in a cool dark cupboard. After the prescribed period of standing, 1 ml. of a 1 per cent. solution of *o*-nitrobenzaldehyde in 50 per cent. ethyl alcohol is added, and the solutions are mixed by gentle shaking. Finally, 2 ml. of a 30 per cent. solution of sodium hydroxide are added, and the solutions shaken once more. The tubes are then allowed to stand for about 15 minutes in diffused daylight, and the colours developed are compared with those produced in standard isopropyl alcohol solutions similarly treated. A convenient standard solution is one containing 2.5 ml. of pure isopropyl alcohol in 100 ml. of 10 per cent. ethyl alcohol. The standard colours are those produced by using 1.0, 1.5, 2.0 ml., etc., of this solution, made up to 10 ml. with 10 per cent. ethyl alcohol.

Under the conditions described, the test will detect with certainty the presence of 0.025 ml. of pure isopropyl alcohol in the 10 ml. of 10 per cent. alcoholic solution used. The method is not so delicate as when applied directly to acetone, owing to the complex nature of the action of bromine on isopropyl alcohol, but the proportion of acetone produced by this method from a given quantity of isopropyl alcohol in a given time under similar conditions appears to be constant.

In routine testing the value of the indications is not appreciably affected by the presence of small proportions of formaldehyde or methyl alcohol. Normal propyl alcohol in this test, however, gives a brownish colour on the addition of soda, probably due to the resinification of propyl aldehyde produced by the treatment with bromine. Although this colour gradually fades, it is liable to interfere with the shade of colour produced from isopropyl alcohol. In the presence of *n*-propyl alcohol a quantitative determination of isopropyl alcohol by this method should only be attempted when the proportion of *n*-propyl alcohol is known, so

that the equivalent quantity of *n*-propyl alcohol may be added to the standards before oxidation with bromine.

In this Laboratory the chief value of the test has been found in its giving a ready qualitative method of examination applicable to a large number of alcoholic solutions at a time.

Where a positive indication is obtained the test is repeated, omitting oxidation with bromine, in order to detect whether acetone is present. Quantitative determinations are then made as described above, if necessary both before and after oxidation. Alternatively, the dichromate oxidation process described later may be employed.

IV. DETERMINATION OF ACETONE, ETHYL ALCOHOL AND ISOPROPYL ALCOHOL MIXTURES.—For the determination of acetone the above-described colorimetric method is suitable, or the well-known Messenger process can be employed. For ethyl alcohol and isopropyl alcohol it was thought that if conditions could be found whereby these could be oxidised completely to acetic acid and acetone, respectively, then the determination of these products would enable the proportions of the alcohols to be calculated. Of the oxidising agents tried, potassium dichromate and sulphuric acid gave the most promising results, especially as it was found that the oxidation could be carried out at room temperature in a closed vessel, thus obviating loss. The behaviour of each of the three substances under various conditions of oxidation was studied.

Oxidation of Ethyl Alcohol.—The factor which is most pronounced in determining the rate of oxidation at room temperature is the proportion of sulphuric acid. With small proportions of sulphuric acid oxidation to acetic acid takes many hours, or even days, whilst with fairly large proportions it is complete in a few minutes. Unless the quantity of acid is extremely large, oxidation does not go beyond acetic acid. Under the conditions finally chosen the time required is less than 15 minutes. After reduction of the excess of dichromate the acetic acid can be steam-distilled and titrated.

Oxidation of Isopropyl Alcohol.—The proportion of sulphuric acid similarly determines the rate of oxidation, which proceeds regularly to acetone; with high proportions of acid the acetone formed is further oxidised. Under the selected conditions the oxidation is complete in 15 to 20 minutes. After reduction of the excess of dichromate the acetone produced can be distilled.

Oxidation of Acetone.—With moderate proportions of sulphuric acid oxidation is extremely slow, but the rate of oxidation increases with the proportion of acid. Under the selected conditions no appreciable action takes place in half-an-hour.

Method of Oxidation.—The concentration of sulphuric acid in the oxidising mixture which gives the best results is 12.5 ml. of concentrated acid per 100 ml. The proportion of potassium dichromate present is not so important, but about 5 grms. per 100 ml. is a suitable quantity. It is convenient to prepare a stock oxidising mixture of double strength to be mixed with an equal volume of the solution to be oxidised.

An aliquot part of the distillate to be tested, containing not more than 1.5 gm. ethyl alcohol or 3 grms. of isopropyl alcohol, is placed in a distillation flask of about 800 ml. capacity and diluted with water to approximately 100 ml. An equal volume of the stock oxidising mixture (10 grms. of potassium dichromate and 25 ml. of conc. sulphuric acid per 100 ml.) is added, and the flask is corked and allowed to stand for 25 to 30 minutes. An excess of ferrous sulphate is added, and the solution is steam-distilled, the contents of the flask being allowed to concentrate to about 100 ml. The concentration should not be carried too far, or the distillate becomes yellowish and gives an acidity not due to acetic acid. This occurs when evaporation has proceeded so far that iron compounds separate in the distilling flask and cause bumping. If the volume of liquid is not reduced below about 100 ml., this condition is completely avoided. The whole of the acetic acid should be in the distillate when about 500 to 600 ml. have been collected, but it is advisable to collect a further 100 ml. in a fresh receiver. The distillate is titrated with normal sodium hydroxide, solid phenolphthalein being used as indicator. The addition of 10 to 20 grms. of common salt makes the end point rather sharper. 1 ml. of *N* alkali = 0.046 gm. of ethyl alcohol = 0.058 ml. of ethyl alcohol = 0.101 ml. of proof spirit. The neutralised solution is then redistilled, the distillate being made up to a known volume and the acetone present determined from the specific gravity of the solution (see following paper) or, if small in amount, colorimetrically. The acetone found represents that originally present, together with that produced from the isopropyl alcohol.

1 ml. acetone = 1.043 ml. isopropyl alcohol.

The following results were obtained by this method:—

Ethyl Alcohol:—10 ml. of a solution of specific gravity 0.97840 (=1.761 ml. ethyl alcohol) oxidised. Acetic acid titration = 30.35 ml. of *N*/1 alkali. Ethyl alcohol = $30.35 \times 0.058 = 1.760$ ml.

Isopropyl Alcohol:—25 ml. of a solution of specific gravity 0.98770 (=2.43 ml. isopropyl alcohol) oxidised. Acetic acid titration = 0.2 ml. of *N*/1 alkali (equivalent to 0.01 ml. ethyl alcohol). The recovered acetone diluted to 100 ml. had specific gravity 0.99748 = 2.28 ml. acetone = 2.38 ml. isopropyl alcohol.

Acetone:—3.98 grms. (=5.00 ml.) pure acetone treated. Acetic acid titration = 0.1 ml. of *N*/1 alkali. The re-distilled acetone, diluted to 100 ml., had specific gravity 0.99467 = 4.96 ml. acetone.

V. NOTE WITH REGARD TO *N*-PROPYL ALCOHOL.—When *n*-propyl alcohol is present the above oxidation method can be used to determine isopropyl alcohol, but not ethyl alcohol. *n*-Propyl alcohol is oxidised by dichromate and sulphuric acid, and, as with ethyl alcohol, the proportion of acid determines the rate of oxidation. The product, however, is not solely propionic acid, but a mixture of that acid and acetic acid. The relative proportion of the two varies with the conditions, the ratio of acetic acid to propionic acid increasing with the proportion of acid. No conditions were found which at room temperature, would give solely

propionic or solely acetic acid. Under the above specified conditions of oxidation *n*-propyl alcohol gives about 70 per cent. propionic acid and 30 per cent. acetic acid. Although the product is a mixture, 1 mol. of *n*-propyl alcohol gives 1 mol. of acid, so that after steam distillation the mixed acid can be titrated; and with *n*-propyl alone present, 1 ml. of *N*/1 alkali = 0.060 grm. *n*-propyl alcohol = 0.0743 ml. *n*-propyl alcohol. With mixtures of ethyl and *n*-propyl alcohols the titration of the acids produced by oxidation may form a useful check of the proportions of the two alcohols, calculated from the strength and refractometer readings of their aqueous solution.

VI. SUMMARY.—1. Comparative Tables are given of the strengths and immersion refractometer readings of aqueous solutions of acetone and of some of the lower alcohols.

2. Provided not more than 10 per cent. by volume of these substances are present in aqueous mixtures, the specific gravities and refractometer readings are approximately additive factors.

3. A rapid method for the detection and colorimetric determination of acetone is given, with an adaptation of the process to the determination of isopropyl alcohol.

4. Conditions are given for the complete oxidation of ethyl alcohol and isopropyl alcohol, respectively, to acetic acid and acetone, with a method for the determination of these products.

The authors desire to thank the Government Chemist for permission to publish this work.

GOVERNMENT LABORATORY,
W.C.2.

The Specific Gravities and Immersion Refractometer Readings of Dilute Mixtures of Acetone and Water.

By JOHN RALPH NICHOLLS, B.Sc., F.I.C.

(Read at the Meeting, December 5, 1928.)

CAREFULLY fractionated commercial acetone was found to contain appreciable quantities of oxidisable material. It was therefore distilled twice from dichromate and sulphuric acid (the second operation showing no appreciable change of colour due to oxidation), the distillate being then shaken with anhydrous potassium carbonate and again distilled. The constant-boiling fraction was shaken with fused calcium chloride for several days, re-fractionated, and the process repeated until the specific gravity was constant. The final product boiled at 56.61–56.64° C. at 775.5 mm. (56.04–56.07° C. at 760 mm.) and had a specific gravity at 60° F./60° F. of 0.7960, and an immersion refractometer reading at 60° F. of 89.7 ($N_D = 1.36098$).

Another sample of acetone was prepared from the sodium iodide compound and was similarly fractionated and dried. The product boiled at 55.65–55.70° C. at 749 mm. (56.05–56.10° C. at 760 mm.) and had a specific gravity at 60° F./60°F. of 0.7960, and an immersion refractometer reading of 89.5 at 60° F. ($n_D = 1.36092$).

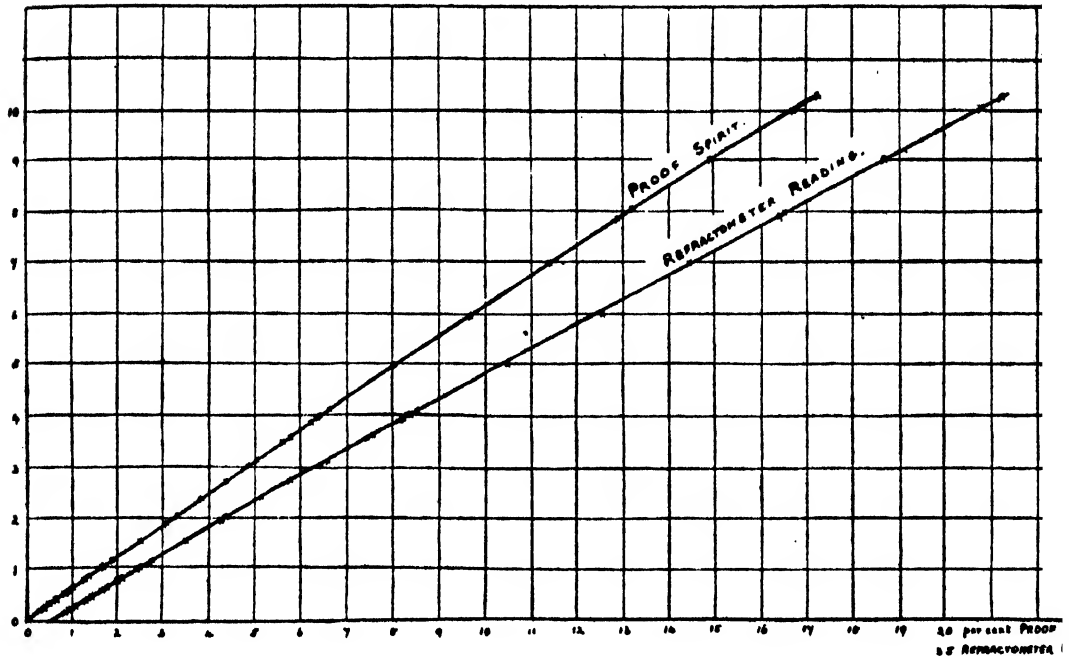
Weighed quantities of each of these products were diluted with water to 100 ml., and the specific gravities and refractometer readings taken. The following were the results obtained:—

ACETONE I.

Acetone, grms. per 100 ml.	Specific gravity	Refractometer reading at 60° F.	Equivalent proof strength from Official Specific Gravity Tables.
	60° F. 60° F.		
0.174	0.99975	15.8	0.29
0.294	0.99958	16.05	0.48
0.476	0.99932	16.35	0.79
0.619	0.99914	16.65	1.00
0.781	0.99891	17.0	1.27
1.170	0.99837	17.75	1.90
1.565	0.99786	18.5	2.50
1.928	0.99737	19.25	3.08
2.379	0.99676	20.15	3.81
2.722	0.99632	20.8	4.35
3.137	0.99576	21.6	5.03
3.520	0.99525	22.4	5.66
3.587	0.99514	22.6	5.80
3.899	0.99478	23.2	6.26
3.964	0.99469	23.3	6.37
4.060	0.99451	23.5	6.60
7.922	0.98973	31.5	12.91

ACETONE II.

Acetone, grms. per 100 ml.	Specific gravity	Refractometer reading at 60° F.	Equivalent proof strength.
	60° F. 60° F.		
0.205	0.99971	15.9	0.34
0.394	0.99943	16.3	0.66
0.570	0.99919	16.7	0.94
0.814	0.99887	17.1	1.31
1.005	0.99858	17.5	1.64
2.020	0.99719	19.5	3.29
3.004	0.99592	21.5	4.82
3.994	0.99464	23.5	6.43
4.972	0.99334	25.5	8.08
5.982	0.99203	27.6	9.78
6.997	0.99081	29.5	11.42
8.015	0.98954	31.6	13.17
9.007	0.98829	33.7	14.96
9.985	0.98706	35.8	16.76
10.238	0.98678	36.2	17.18



The following figures were interpolated from the plotted results:—

Acetone, grms. per 100 ml.	Equivalent proof strength.	Refractometer reading at 60° F.
0	0	15.5
1	1.63	17.45
2	3.24	19.4
3	4.83	21.35
4	6.45	23.4
5	8.12	25.5
6	9.80	27.65
7	11.44	29.6
8	13.15	31.55
9	14.93	33.7
10	16.73	35.75

GOVERNMENT LABORATORY,
W.C.21

The Wijs Method as the Standard for Iodine Absorption.

By J. J. A. WIJS, Ph.D.

(Read at the Meeting, December 5, 1928.)

AMONG the subjects discussed at the ninth Conference of the International Union of Pure and Applied Chemistry at the Hague was the standardisation of the determination of the iodine value.

The discussion resulted in a resolution that the method devised by me should have the preference, especially in forensic cases, and that it should be accepted as the official method. In the literature on this subject there are two papers, the contents of which seem to be incompatible with this conclusion.

I. Schmidt-Nielsen, referring to the method in his *Vergleichende Untersuchungen*,* observed: "Besides the addition, a substitution also takes place. For this reason one can never obtain correct iodine values, and the method is altogether unsuitable for all scientific work."

Nielsen compares different methods of determining the iodine value by following the course of the iodine fixation. For this purpose he stops the reaction after 2, 6 and 24 hours, and represents the calculated iodine values by a graph. Then, from the results, he postulates that the curve, drawn through the three points, must show a horizontal portion, which would indicate a cessation in the iodine absorption. Not finding such a stoppage indicated in the line he drew for the Wijs reagent, he concludes that there must be substitution as well as addition. This conclusion is somewhat hazardous, but much more important is the fact, that the observation, the basis of the conclusion, is defective.

As long ago as 1899 I made and published (*Chem. Rev. Fett. Ind.*, 1899, 6, 5; *ANALYST*, 1899, 24, 94) similar experiments. I reproduce here Table VII of that paper.

Time.	Arachis oil.			Linseed oil.		
	N/10 thiosulphate c.c.	Free halogen in terms of N/10 thiosulphate. c.c.	Velocity in terms of N/10 thiosulphate. c.c.	N/10 thiosulphate. c.c.	Free halogen in terms of N/10 thiosulphate. c.c.	Velocity in terms of N/10 thiosulphate. c.c.
0	36.25	—	—	37.89	—	—
1 min.	—	26.88	562.2	—	27.69	612.6
5 "	—	26.81	1.05	—	27.54	2.25
15 "	—	26.77	0.24	—	27.52	0.12
1 hour	—	26.77	0.00	—	27.50	0.02
2 "	—	26.77	0.00	—	27.50	0.00
6 "	36.25	26.75	0.005	—	27.47	0.01

* Edited by J. Dybwad, Kristiania, 1923.

It is evident that the stoppage required by Nielsen appears here very clearly; with arachis oil after a quarter of an hour, and with linseed oil within an hour. Nielsen, however, could not detect this stoppage, for the simple reason that he did not end his first experiment until after two hours.

It is hardly surprising that in such a mixture as the one in question a slow diminution of the free halogen will, in the long run, occur. If, however, during the short time of the experiment itself, these secondary reactions are so small as not to change perceptibly its result, the method is not affected. The table given above proves clearly that this is the case here.

In studying Nielsen's curves, one should bear in mind that only three points in each curve have been fixed by experiment. Nielsen, in drawing these curves, tacitly assumed that no stoppage or irregularity had occurred. As regards my reagent, my experiments clearly prove that this assumption does not agree with the facts.

II. The *Kritisch-experimentelle Untersuchungen* of Weiser and Donath (ANALYST, 1914, 28, 65) also appear not to support my method. These authors determined the iodine value of pure unsaturated fatty acids, and failed to obtain the theoretical values, when using the Wijs reagent.

I regret to have to say, however, that these experiments, so far as they relate to my method, involve a fundamental error. Weiser and Donath state explicitly that they prepared the reagent according to Lewkowitsch's formula, using 9.4 grms. of iodine trichloride and 7.2 grms. of iodine.

This is an unfortunate error in Lewkowitsch's excellent book, which was corrected in the next edition, but, unfortunately, passed in the French translation by Bontoux. To convert 9.4 grms. of iodine trichloride into monochloride 10.2 grms. of iodine are required.

Weiser and Donath made their experiments with a solution containing a large quantity of iodine trichloride, whereas it is known that even a small quantity makes the solution unstable and causes secondary reactions. The experiments of Weiser and Donath are therefore valueless as adverse criticism of my method.

In 1899 I determined the iodine values of erucic, brassidic and elaidic acids, and obtained the theoretical values. Analogous results can be obtained with the other fatty acids present in natural oils and fats, as is clearly shown in the interesting paper of Boeseken and Gelber (*J. Chem. Ind.*, 1927, B, 427), the study of which I warmly recommend to everyone interested in the determination of iodine values.

It may be useful to add some details to amplify the general directions for using the method, which were published in the Report of the Conference (*loc. cit.*). The best method of preparing the reagent is to dissolve about 9 grms. of iodine trichloride in one litre of glacial acetic acid of at least 99 per cent. strength. If the liquid is to be kept in a cold place, where it could crystallise, a mixture of 300 c.c.

carbon tetrachloride and 700 c.c. acetic acid may be used instead of one litre of acetic acid.

Exactly 5 c.c. of this solution are taken, and its halogen content determined by means of $N/10$ thiosulphate solution, after adding potassium iodide and water. The bulk of the solution is treated with 10 grms. of pulverised iodine and shaken to make it dissolve. When almost all the iodine is dissolved, exactly 5 c.c. are again taken, and the halogen content determined. As soon as this is found to be one-half more than that found by the first determination the solution is filtered into a bottle provided with a tightly fitting stopper. It is preferable to exceed slightly this limit of one-half more, as this ensures that no iodine trichloride remains in the finished reagent, the effect of which would be to make this preparation unstable and cause secondary reactions when it was used for the determination. If desired, the reagent thus prepared may be diluted with acetic acid to exactly $N/5$ strength.

The acetic acid and carbon tetrachloride must be absolutely free from oxidisable matter; this is controlled by warming one or two c.c. of each liquid with some concentrated sulphuric acid and a drop of a saturated dichromate solution. A green tinge should not be noticeable, even after prolonged standing. It is necessary to be very punctilious on this point, in order to get a stable solution; 0.46 per cent. of ethyl alcohol, oxidised to aldehyde, would be sufficient to effect complete reduction of all the halogen present in an $N/5$ solution. Kept in a well-closed bottle, in the dark, the solution remains in good condition for years.

It must be borne in mind that its coefficient of expansion by heat is rather high (0.00115); thus, for 25 c.c., a difference in temperature of 1°C. makes a difference in the titration with $N/10$ thiosulphate of 0.06 c.c.

The quantity of oil or fat to be taken for a test should be so measured that not more than 30 per cent. of the halogen present in the 25 c.c. of the solution added is absorbed. This quantity of oil is dissolved in a few c.c. of carbon tetrachloride before the 25 c.c. of the iodine solution are added.

After half-an-hour to two hours, according to the degree of unsaturation of the fatty substance, the non-absorbed halogen is titrated.

The Natural Occurrence of Boron Compounds in Fruits and Vegetable Products.

BY A. SCOTT DODD, B.Sc., F.I.C., F.R.S.E.

(Work done under the Analytical Investigation Scheme.)

(Read at the Meeting, December 5, 1928.)

IN a recent publication by the author (ANALYST, 1927, 52, 459) reference was made to the existence of boron compounds as normal constituents of various vegetable substances. It was then shown that boron compounds are present in cacao and cacao products to quite an appreciable extent. The present investigation was undertaken with a view to ascertain to what extent boron is present in other vegetable commodities, and to determine what quantitative margin should, in general, be allowed in differentiating between "natural" and "added" boron compounds in commercial vegetable products. G. Bertrand and H. Agulhon (*Compt. rend.*, 1914, 158, 201) determined boron compounds in a large number of fruits and vegetables by means of a colorimetric method devised by themselves. In most cases, however, these results are much lower than those found by the author in the present investigation.

METHOD OF ANALYSIS.—The boric acid was, in each instance, determined by the author's modification of Thomson's method described in the previous publication (*loc. cit.*). As, however, the quantity of boric acid was very small, it was considered expedient to use about 40 grms. of the sample for each determination, and to carry out the titration by means of a 10 c.c. burette of narrow bore, so that the readings could readily be made to one hundredth of a c.c. In the case of those substances which contained little fat, ether extractions were dispensed with, while in every instance care was taken to ensure the presence of a distinct excess of alkali before igniting.

SELECTION OF SAMPLES.—Keeping in view the fact that "added" boron compounds constitute an infringement of the Public Health (Preservatives) Regulations, 1925, special attention was paid to those vegetable substances which form the constituents of manufactured products. Currants and raisins, for example, enter into the manufacture of cakes, buns, mince meat, wines, etc. Various fruits also enter into jams, cakes and sauces, while spices and flavourings, such as almond and coconut, were also regarded as likely sources of boron compounds. The field for such an investigation is, therefore, very wide; and though no claim to exhaustiveness can be made, this investigation covers a wide range of articles and indicates that the quantity of boron compounds occurring naturally

in vegetable products is comparatively small, and therefore not likely to be confused with those quantities, which would require to be added for preservative purposes.

CURRENTS AND RAISINS.

Variety.	ACTUAL.			DRIED.		
	Boric acid. Per Cent.	Moisture. Per Cent.	Ash. Per Cent.	Organic matter. Per Cent.	Ash. Per Cent.	Boric acid. Per Cent.
Vostizza currants	0.014	11.90	2.45	97.22	2.78	0.017
Australian currants	0.013	5.00	2.05	97.84	2.16	0.014
B.P. Patras currants	0.010	11.15	2.35	97.36	2.64	0.011
Spanish muscatels	0.015	20.70	1.80	97.73	2.27	0.020
Spanish muscatels	0.012	12.45	2.65	96.98	3.02	0.014
Smyrna sultanas	0.018	13.90	2.15	97.50	2.50	0.022
Australian sultanas	0.022	15.15	1.75	97.94	2.06	0.026
Smyrna sultanas	0.012	14.10	2.80	96.51	3.49	0.014
Valencia raisins	0.010	10.50	2.00	97.77	2.23	0.011
Californian raisins	0.013	14.85	2.40	97.18	2.82	0.016

These results show that both currants and raisins contain small, but appreciable, quantities of boron compounds. The amount in the dried fruits varies from 110 to 260 parts per million by weight, and, so far as these samples show, there is no evidence to prove that the Valencia raisins and the sultanas, which are subjected to "dipping" in process of preparation for the market, contain less boric acid than the currants and raisins which are not dipped. While the quantity of boric acid in each sample is admittedly too small to be of much use for the purpose of preservation, it is interesting to note that all the above currants and raisins contain more than 100 parts per million of boric acid.

DRIED FRUITS.

Variety.	ACTUAL.			DRIED.		
	Boric acid. Per Cent.	Moisture. Per Cent.	Ash. Per Cent.	Organic matter. Per Cent.	Ash. Per Cent.	Boric acid. Per Cent.
Australian apricots	0.022	22.60	3.75	95.16	4.84	0.029
Californian apricots	0.023	20.40	3.65	95.41	4.59	0.030
Persian dates	0.006	19.30	1.75	97.83	2.17	0.008
Crystallised cherries	0.014	17.85	1.25	98.48	1.52	0.018
Turkish figs	0.006	22.10	3.25	95.83	4.17	0.008
Australian peaches	0.025	16.35	3.15	96.24	3.76	0.030
Californian peaches	0.022	19.25	3.50	95.54	4.46	0.028
French prunes	0.003	15.85	1.80	97.86	2.14	0.004
Californian prunes	0.003	17.50	1.75	97.88	2.12	0.004
French prunes	0.003	16.40	1.90	97.73	2.27	0.004
Dried pears	0.008	19.00	1.45	98.21	1.79	0.011
Dried apple rings	0.006	18.40	1.25	98.47	1.53	0.008

In the above list of miscellaneous dried fruits the boric acid content of the dried sample is shown to vary from 40 parts per million, in prunes, to 300 parts per million, in apricots and peaches. It is noteworthy that the Californian prunes contain much less boric acid than the apricots and peaches from California, but little can be deduced from this fact, as the districts may be too far from one another to show definitely that the apricot and peach trees take up more boron compounds from the soil than the plum trees, although these results certainly suggest that such an occurrence is probable. The above results show, however, that quite appreciable quantities of boron compounds exist as natural constituents of apricots and peaches, and must therefore be allowed for in jams, tarts, and other products manufactured therefrom.

FRESH FRUITS.

Variety.	ACTUAL.			DRIED.		
	Boric acid. Per Cent.	Moisture. Per Cent.	Ash. Per Cent.	Organic matter. Per Cent.	Ash. Per Cent.	Boric acid. Per Cent.
Belgian black currants	0.005	81.50	0.55	97.03	2.97	0.030
Belgian red currants	0.005	85.10	0.90	93.96	6.04	0.033
German cherries	0.003	84.40	0.30	98.08	1.92	0.024
French cranberries	0.006	88.80	0.25	97.77	2.23	0.055
Belgian gooseberries	0.003	88.85	0.35	96.86	3.14	0.028
Dutch tomatoes	0.005	94.85	0.45	91.27	8.73	0.109
Danish cranberries	0.003	90.50	0.15	98.42	1.58	0.039

Although the actual amount of boron compounds found in these samples of fresh fruit is very small, namely, varying from 31 to 62 parts per million expressed as boric acid, it will be observed that fairly high figures are obtained when these results are calculated on the dry sample. The quantity of boric acid in the dry substance varies from 240 to 1090 parts per million; and although apparently of alarming magnitude, when considered with reference to the Public Health (Preservative) Regulations, 1925, is not likely to be nearly so large in any products prepared therefrom, as most of the latter contain a considerable proportion of water. On comparing the amounts of boric acid in the fresh fruits and dried fruits calculated on the dried samples, it will be observed that the fresh fruit results are, on the whole, much higher. This, however, may be largely, if not entirely, accounted for by a loss of boric acid occurring during the drying of acid fruits without the presence of an alkaline fixing agent.

A. Hebebrand (*Z. Unters. Nahr. Genussm.*, 1902, 5, 1044-1049) found minute quantities of boric acid in orange juice and lemon juice, amounting to 4 and 6 mgrms., respectively, per litre. The Report of the Government Chemist for the year ending in March, 1928, shows that a number of oranges were tested to ascertain if boric acid were present in the edible portions of the fruit, and that mere traces only were found therein. These two investigations and results are of

especial interest, in view of the fact that Australian growers sterilise the skins of citrus fruits before export.

SPICES AND FLAVOURINGS.

Variety.	ACTUAL.			DRIED.		
	Boric acid. Per Cent.	Moisture. Per Cent.	Ash. Per Cent.	Organic matter. Per Cent.	Ash. Per Cent.	Boric acid. Per Cent.
Californian almonds	0.014	3.90	2.65	97.24	2.76	0.015
Dutch caraway seeds	0.012	11.50	7.25	91.81	8.19	0.014
Ground cinnamon	None	—	—	—	—	None
Ground coconut	0.001	3.35	1.30	98.65	1.35	0.001
Ground ginger	None	—	—	—	—	None
Black pepper	0.014	11.85	4.25	95.18	4.82	0.016
Mixed spice	0.008	9.50	5.00	94.48	5.52	0.010

With the exception of almonds and coconut, none of the above spices and flavourings occurs in large proportion in any manufactured product. The quantity of boric acid in no instance is high, and is so small (if present) as to be undetectable in cinnamon and ginger, while in coconut it is practically negligible. One would expect to find less boron compounds in the fibrous than in the more succulent portions of a plant, and the above results certainly tend to support this theory, and show that in the vegetable kingdom boron compounds are more plentiful in fruits than in stem structures.

VEGETABLE PRODUCTS.

Variety.	ACTUAL.			DRIED.		
	Boric acid. Per Cent.	Moisture. Per Cent.	Ash. Per Cent.	Organic matter. Per Cent.	Ash. Per Cent.	Boric acid. Per Cent.
Indian relish	0.001	67.50	1.60	95.08	4.92	0.006
Tomato ketchup (1)	0.003	63.40	3.90	89.34	10.66	0.008
Tomato ketchup (2)	0.001	64.50	4.10	88.45	11.55	0.005
Indian mango chutney	0.008	34.05	3.25	95.00	5.00	0.012
Fruit cake (1)	0.011	28.50	1.25	98.25	1.75	0.016
Mince meat	0.009	18.40	1.65	97.98	2.02	0.011
Green tomato chutney	0.003	75.40	0.40	98.38	1.62	0.015
Fruit cake (2)	0.013	25.70	1.45	98.05	1.95	0.017

The above results show the boric acid content of certain classes of manufactured vegetable products, which one would expect, from their concentrated nature, to contain a proportion of boron compounds approximating to the maximum. In no instance, however, was the quantity of boric acid found to be high; it varied from 19 parts per million in relish and ketchup to 130 parts per million in fruit cakes, which were largely composed of currants and other dried fruits and spices. Even allowing for the maximum limits of variation produced by different degrees of dryness, the amount of boric acid is still small, as the water-free product, which

would never be found in practice, is shown to contain only 170 parts per million of boric acid.

WINES AND VINE PRODUCTS.

Variety.	Boric acid. Per Cent.	Extract. Per Cent.	Ash. Per Cent.
British wine (1)	0.003	14.60	3.80
British wine (2)	0.002	15.15	4.30
Spanish grape juice	0.024	44.50	0.75
Greek grape juice	0.016	47.80	0.50
South African grape juice	0.018	70.80	0.60

For many years it has been known that boron compounds exist as natural constituents of wines and vine products. H. Jay and Dupasquier (*Compt. rend.*, 1895, 260) found Bordeaux and Burgundy wines to contain amounts of boric acid varying from 0.010 to 0.022 gm. per litre. The above results are expressed in parts by weight, and are similar, though somewhat higher, than those found by these investigators.

The vine is the main source of natural boric acid in the majority of wines, and the above results indicate that the quantity of boric acid existing naturally in wines is very small, and amounts merely to 10–30 parts per million. Grape juice, which is imported from various countries as a basis for the manufacture of British wines, is a concentrated article, and therefore contains quite an appreciable quantity of boric acid. The results given show considerable variation in the boric acid content, and the variation is even more pronounced when the figures are calculated to the same concentration of extract. It is, however, clearly shown that the quantity of natural boron compounds expressed as boric acid is much less than would be likely to be added to prevent the juice fermenting.

CONFIRMATORY TEST FOR BORIC ACID.—It was observed in carrying out the final titrations in the boric acid estimation (*ANALYST*, 1927, 52, 464) that the neutralised solution, free from carbonic anhydride and phosphates, gave a pink coloration when mannitol was added (Sofnol Indicator No. 1 being present as the indicator). No pink colour was given, when boric acid was absent, and the depth or intensity of pink was greater or less according to the quantity of boric acid present.

In the fruits and samples in which minute quantities only of boron compounds were present the pink reaction was found to be very faint, whereas in other substances and fruits containing a larger quantity of boron compounds the pink reaction was very distinct.

Each of the substances under examination in this investigation was carefully tested by the sensitive turmeric paper test detailed by the author (*ANALYST*, 1927, 52, 465). It was found that in each instance this qualitative test was satisfactorily confirmed in the course of the investigation by the intensity of the pink reaction, which acted as a useful confirmatory test.

GENERAL CONCLUSIONS.—In surveying the foregoing analytical results it will be observed that, in the actual samples tested, the amount of boron compounds, expressed as boric acid, varies from none to 0.025. Fuller investigation would require to be made before one could arrive at a definite maximum, but, so far as the results of this investigation go, it would appear that no product manufactured from mixtures of fruits and spices would be likely to contain more than 0.03 per cent. of boron compounds, expressed as boric acid. This amount is, as already shown, very much less than the minimum quantity of boric acid which would be added as a preservative, as no one would be likely to add less than 0.15 per cent. of boric acid with any hope of ensuring efficient keeping qualities. Even allowing a substantial margin for all possible variations, it would appear that if any article of food were found to contain more than 0.1 per cent. of boric acid, it would be reasonable to conclude that the article contained added boron compounds.

The wide geographical distribution of boron compounds is shown by the presence of boron in the various vegetable products mentioned in this and the previous investigations. It would, therefore, appear that boron compounds exist in practically all soils, and it is quite conceivable that in districts where it is very abundant the vegetation grown thereon will contain a larger amount than the vegetation grown on soils which contain minute traces only of boron compounds. Certain plants may, of course, possess greater powers of assimilating boron compounds than other plants, as researches in this subject have shown that, up to certain amounts, boron compounds assist growth and development, though larger quantities invariably retard the growth.

Special care has been taken throughout this investigation to ensure that the results obtained are reliable. It was found that, in undertaking the determination of such small quantities of boric acid, great care and strict adherence to technique was necessary in order to avoid the introduction of minute but nevertheless appreciable errors. The modified Thomson's process, though somewhat laborious, was adhered to throughout, and was found to give very satisfactory results.

In conclusion, the author would like to acknowledge his indebtedness to the Scottish Federation of Grocers and others who have kindly supplied him with reliable samples necessary for this investigation.

DISCUSSION.

The PRESIDENT said that he was a little sceptical about the accuracy or reality of these small quantities when they depended upon the titration method by *N*/10 sodium hydroxide solution. The method used was the modified "Thomson," which was really known as the Government Laboratory method, but he understood that the Government method was brought forward to deal with large quantities of boric acid. His experience had been that with many products there was always a slight blank attaching to this method, and the old Thomson method gave a similar blank, due to small quantities of phosphoric acid.

Dr. B. S. EVANS said that he thought that metallurgical analysis might throw a little light on the question. He had carried out many experimental determinations of boron in copper, and in this case, as it was impossible to burn off the copper, it had to be precipitated; this was done with sodium hydroxide,

which caused a considerable concentration of salts in the liquid. Under these conditions he found blanks varying from 0.3 to 1.0 c.c. of *N*/10 sodium hydroxide solution, and as the circumstances entirely precluded the possibility of the presence of phosphates, and rendered any appreciable amount of carbon dioxide unlikely (the acid solutions had been boiled for a considerable time under a reflux condenser), he had attributed the blank to silica. This was rendered more probable by the fact that sodium hydroxide dissolved in porcelain gave a lower blank than that in glass, and in platinum lower still. He found the error in his determinations to be ± 0.3 mgrm. He did not know if glycerin was still used in the Thomson process, but he found mannitol greatly superior. He wondered whether the author had followed up the colour reaction quantitatively, as he believed a colorimetric method would be very valuable.

Mr. A. MORE agreed that there was a blank in the Thomson method, often amounting to 0.1 or 0.15 ml.; it was due to the carbonic acid not having been entirely removed by boiling. He doubted some of the figures given by the author, and wondered whether there was not some constant error both in these figures and in the author's previous results on cocoa. As an example of a titration error, he cited an instance where, some years ago, a sample of cocoa had been examined by this process and reported to contain a large amount of boric acid. The ash of the cocoa, however, did not give an indication of boric acid with turmeric, and contained no boric acid. The cause of the error was traced to the fact that calcium chloride had not been added in sufficient quantity before the neutralisation stage. Cocoa ash contained a very much larger proportion of magnesium than of calcium, and magnesium phosphate did not precipitate so completely as calcium phosphate. At the stage of the process where the phosphate should have been precipitated completely some remained soluble as magnesium phosphate, and caused a very pronounced difference between the neutral points to the two indicators, which was reported as boric acid. In most cases since then he had obtained a quantitative confirmation of the amount of boric acid by a colorimetric method before reporting the titrimetric result.

Mr. CHASTON CHAPMAN remarked that the figures given by the author appeared to refer only to land fruits. He might, however, remind the meeting that he had shown in a recent communication that traces of boric acid were present in agar and in other sea-weeds. He felt strongly that it was unwise to attach too great importance to very small titration numbers, and he himself would not feel satisfied unless he confirmed such results by some specific test. Probably the author had done so. He felt that the practical value of the communication was reduced to some extent by the fact that quantities such as the author had found could not properly be regarded as significant in connection with analyses made under the Sale of Food and Drugs Acts. He contended that the real object of those Acts was to protect the public without harassing the trader, and therefore there would be no necessity for the Public Analyst to report the presence of traces, even having full regard to existing Regulations.

Dr. MONIER-WILLIAMS, while agreeing with the views expressed by the last speaker, said he was prepared to accept the figures published, but at the same time there was often some uncertainty in the case of imported fruits, *e.g.* oranges, as to whether they had been treated with boric acid in the country of origin. He could confirm the amount found in Australian sultanias, as he had examined a sample sent from Australia House, which was guaranteed not to have been treated.

Professor W. H. ROBERTS said that he could confirm the presence of small amounts of boric acid in currants, but that he had evidence that in some cases, at all events, it was due to the currants having been washed with boric acid.

Mr. A. E. PARKES said that the paper had cleared up a small mystery which had been bothering jam manufacturers for some time. Unaccountable traces of boric acid had frequently been found in jams and mincemeat. During the last year he had examined half-a-dozen samples of jam which contained 1-2 grains per pound of boric acid—an amount which roughly corresponded with that found by the author in fruits. During the past season he had examined several samples of mincemeat, all of which gave a strong boric acid reaction with turmeric paper.

The PRESIDENT asked Dr. Cox if he would kindly reply in the absence of the author.

Dr. COX stated that much of the criticism was anticipated, and Mr. Scott Dodd had sent samples to him, and he had examined them for boric acid. With regard to the blank—he could state definitely that it did not exceed one drop from an ordinary burette. Mannitol was certainly very sensitive, and gave more definite results than glycerin. He was afraid he could not say what "Sofnol No. 1" was.

With regard to the point raised by Mr. More, it was expressly stated by Mr. Scott Dodd that excess of calcium chloride should be added before filtering off.

Two samples of apricots examined by Mr. Scott Dodd and Dr. Cox gave the following percentage results:

Mr. Scott Dodd	..	0.0222	Mr. Cox	..	0.0186
		0.0236			0.0217

and in a number of other samples quantities were of the same order.

It was really essential, in dealing with small quantities, to burn off the carbon completely. When one considered how absorption carbons was made, it would be realised that exactly the same thing was done in this process, and therefore the carbon had absorptive power, and it was essential to burn it off. It was rather tedious in the case of the necessarily large sample of dry fruit, but to get accurate results it must be done. Neglect to do this might explain lower results.

Mr. Scott Dodd pointed out that qualitative confirmation of the presence of boric acid had been obtained.

ADDENDUM.—The point raised by Prof. W. H. Roberts is one of considerable importance, as the value of the results obtained in this investigation depends very largely upon the freedom of these samples from "added" boric acid. The subject of the treatment and preparation of dried fruits has been carefully investigated, and the Secretary of the Scottish Federation of Grocers, who supplied a large number of the samples, and has a very wide and intimate knowledge of these matters, stated emphatically that boric acid is never used in the preparation of dried fruits for the market. Sultanas, apricots, peaches and prunes are commonly treated with sulphur dioxide, but never with boric acid. Dried fruits are treated with preservative substances for two reasons only: to improve their appearance or to kill insects. Boric acid would do neither of these things, and there would therefore be no sense or reason in treating dried fruits with boric acid solutions.

Special care was taken in the selection of the samples used in this investigation, and there is little or no doubt that all the boric acid found therein has been due to its natural occurrence in the plants from which they spring.

With regard to the suggestion that "Sofnol" might be used as the basis for a colorimetric determination of boric acid, it is doubtful if anything would be gained thereby. The mannitol and sofamol colour with boric acid solutions can only be of reliable depth when other acids and phosphates have been eliminated, so it is really more satisfactory to titrate the boric acid than to try to match coloured solutions.—A. SCOTT DODD.

A Method for the Determination of Traces of Antimony in Copper and its Alloys.*

S. G. CLARKE, B.Sc., A.I.C., AND B. S. EVANS, Ph.D., F.I.C.

EVANS published some time ago (*ANALYST*, 1922, 47, 1) a method for the determination of small amounts of antimony in copper and brass; this method, whilst giving fairly good results, had certain objectionable features:

(a) The copper was removed as a sponge by treatment of the sulphate solution with sodium hypophosphite. This process worked well with samples of fairly pure copper, but led to complications and probable loss of antimony in presence of any considerable amount of tin. Moreover, we have latterly found that sodium hypophosphite is liable to be contaminated with an unidentified impurity, which leads to loss of antimony. Further, should the hypophosphite used contain chlorides, as did certain samples of this salt which we have examined, a precipitation of some antimony on the copper sponge would certainly take place.

(b) The arsenic had to be removed completely, owing to the antimony being finally determined colorimetrically as sulphide. This was effected by boiling the chloride solution, after removal of the copper, as mentioned, with sodium hypophosphite, and was quite satisfactory with copper samples; but, as one of us has recently found (Clarke, *ANALYST*, 1928, 373), arsenic cannot be separated quantitatively in presence of stannic salts by precipitation with hypophosphite. This fact would also render the procedure inaccurate when applied to a bronze containing any arsenic.

(c) The traces of copper, bismuth, etc., remaining in the solution obtained by stripping the deposited antimony from the copper after deposition by the Reinsch method, were removed by a tedious, and not too satisfactory, separation with zinc sulphide.

(d) The final colorimetric determination was carried out on a colloidal solution of antimony sulphide. The colour obtained was entirely ruined by any trace of copper, bismuth, etc., which had not been removed by the preceding operation, or rendered too intense by any arsenic which escaped precipitation by sodium hypophosphite.

In 1928, one of us published (Clarke, *ANALYST*, 1928, 373) a method of colorimetric determination of small quantities of antimony, which was a great improvement on the sulphide method, being unaffected by relatively large amounts of tin and arsenic.

Subsequent to the publication of the method for determining antimony in copper, one of us showed (Evans, *ANALYST*, 1923, 48, 264) that, whilst copper in

* Communication from the Research Department, Woolwich.

the cupric state is fatal to the Reinsch reaction, cuprous copper is not. The line of attack, therefore, which led to the present process was:—

- (a) Reduction of the copper to the cuprous state in hydrochloric-sulphuric acid solution. This was effected simply by adding sodium hypophosphite.
- (b) Deposition of the antimony on copper by the Reinsch reaction.
- (c) Determination of the antimony in the solution obtained by stripping the Reinsch film with sodium peroxide, by the method mentioned above.

The full method is as follows:—Five grms. of the sample are dissolved in 30 c.c. of dilute sulphuric acid (1:3) and 15 c.c. of concentrated nitric acid, and evaporated until the sulphuric acid fumes strongly. This may be accomplished safely and quickly by placing the beaker on an asbestos pad on a hot plate till fumes of sulphur trioxide begin to be evolved, and then removing it to the bare plate. The residue, after cooling, is dissolved in 150 c.c. of water, 150 c.c. of concentrated hydrochloric acid (sp. gr. 1.18) are added, followed by 10 grms. of sodium hypophosphite, and the solution is boiled for 10 minutes.

In the absence of any appreciable amount of arsenic (which is generally the case) the liquid may be treated at once by the Reinsch method, as below. If a brownish-black precipitate appears during this boiling (due to arsenic), the liquid must be boiled for a further 20 minutes, cooled somewhat, and well shaken after the addition of 20 c.c. of benzene to coagulate the precipitated arsenic. It is filtered through a wet filter paper, which is washed with the minimum of hot water and rejected. This treatment removes the greater part of the arsenic in the case of all metals not containing a large amount of tin; although arsenic does not interfere in the colorimetric method, its removal, when present in more than small amounts, is advantageous, inasmuch as arsenic depositing with antimony in the Reinsch test tends to weaken the film and cause it to become detached from the copper.*

In the case of a tin bronze, 10 grms. of oxalic acid are dissolved in the hydrochloric acid solution before adding the hypophosphite. In general, a white turbidity is produced which may be ignored; after about 30 minutes' boiling during the Reinsch process this turbidity disappears, yielding a perfectly bright solution.

A piece of pure electrolytic copper foil, about 20×2.5 cm., is rolled into a flat spiral, as open as is consistent with its being dropped into the flask containing the solution under examination; it is cleaned by warming gently with nitric acid (sp. gr. 1.2), rinsed with water and dropped into the solution, which is then boiled gently for two hours. (It is desirable that the coil should stand upright, not lie on its side.) At the end of this time the coil is lifted out of the boiling liquid by means of a hooked glass rod; rinsed *quickly* by plunging into a beaker of water, and placed *without delay* into a small beaker of diameter only slightly greater than that of the coil; it is covered with distilled water, and about 1 grm. of sodium

* In practice, we have not met with tin bronzes containing notable amounts of arsenic; we have therefore not found it necessary to introduce any modification of the process to meet this case.

peroxide is at once added. After standing for five or ten minutes the beaker containing the coil is warmed gently until the coil becomes darkened with a layer of oxide. If too much time has not been allowed to elapse between withdrawing the coil from the boiling acid solution and adding the peroxide, the antimony should now be completely removed from the copper, together with any bismuth and arsenic that was present and a little copper. The liquid is now poured off into a small flask, and the coil and beaker rinsed in twice with distilled water; the coil should be immersed in dilute sulphuric acid, which removes the film of oxide and shows up any antimony which may have escaped stripping. In the rather *unlikely* event of antimony having been incompletely stripped, the stripping process with peroxide must be repeated, and the solution added to that obtained from the first stripping.

The solution containing the antimony is now treated with a rapid current of hydrogen sulphide for 15 seconds, and the flask allowed to stand on a water bath for about half-an-hour; the precipitated copper and bismuth sulphides are then filtered off through a small, close-pressed, pulp filter, and lightly washed with 1 per cent. ammonium nitrate solution; 5 to 6 c.c. of concentrated sulphuric acid are added to the filtrate, and it is evaporated until fumes of sulphur trioxide begin to be evolved, a few drops of nitric acid being added during the latter part of the evaporation. The sulphuric acid solution of antimony is taken up with 15 c.c. of water, heated just to boiling point and cooled; the antimony in this solution is determined colorimetrically as follows:—

Into a 10 c.c. Nessler glass are put reagents in the order named: 10 c.c. of 1 per cent. gum arabic, 5 c.c. of 20 per cent. potassium iodide, 1 c.c. of 10 per cent. aqueous pyridine, 1 c.c. of a dilute solution of sulphur dioxide (one tenth saturated), 60 c.c. of cold dilute (1:3) sulphuric acid. The antimony solution, obtained as described above, is now added, after filtration if necessary, through a small filter paper, the beaker being rinsed in with not more than 5 c.c. of water; the whole is well stirred with a glass rod. Standard antimony solution (0.0001 grm. Sb. per c.c.) is run into another Nessler glass containing similar quantities of reagents (*except that 80 c.c. of 1:3 sulphuric acid are used instead of 60 c.c.*) until the colours match after the solution has been well stirred. A final adjustment is made just before the final colour-match, by adding a small quantity of water to make the volumes in the Nessler glasses equal. The colorimetric comparison is made by viewing the tubes vertically over a white tile inclined at an angle to act as a light reflector.

The standard antimony solution contains 0.2764 grm. of tartar emetic in 1 litre of 10 per cent. sulphuric acid.

If more than 10 c.c. of this standard solution have to be added the colour obtained is too deep for accurate comparison; if the amount of antimony present is still greater, a turbidity is produced. In this case 20 c.c. of the solution are withdrawn from the Nessler glass into another one, similar quantities of reagents are added as in the first instance; any turbidity thereupon disappears, and the colour is matched with fresh standard. It is preferable, however, in this colorimetric method that the amount of antimony should not exceed 0.0005 grm.; in this, as

in almost all other colorimetric work, accuracy begins to fall off when the colour developed becomes unduly deep. Few of the ordinary copper alloys contain more than the above amount in a sample weight of 5 grms., so that subdivision of the solution, as mentioned above, or reduction of the sample weight taken, is rarely necessary.

Trials of the above process made on samples of copper (with and without arsenic), bronze, brass and cupro-nickel, to which varying amounts of antimony had been added (as a standard solution, to the metal in a beaker before dissolving) gave the following results.

COPPER.

Copper taken.	Antimony added.	Antimony solution required.		Antimony found.	Antimony	
Grms.	Grm.	Total. c.c.	Nett. c.c.	Grm.	Added. Per Cent.	Found. Per Cent.
5.0	Blank	0.1	—	—	—	—
5.0	0.00005	0.6	0.5	0.00005	0.001	0.001
5.0	0.00010	1.05	0.95	0.000095	0.002	0.0019
5.0	0.00030	3.0	2.9	0.00029	0.006	0.0058
5.0	0.00050	5.1	5.0	0.00050	0.010	0.010
5.0	0.0010	10.1	10.0	0.0010	0.020	0.020

ARSENICAL COPPER.

Copper taken.	Arsenic added.	Antimony added.	No. of c.c. required.		Antimony recovered.	Antimony.	
Grms.	Per Cent.	Grm.	Total.	Nett.	Grm.	Added. Per Cent.	Found. Per Cent.
5.0	—	Blank	0.1	—	—	—	—
5.0	0.5	0.0003	3.05	2.95	0.00030	0.0060	0.0060
5.0	0.2	0.0003	2.90	2.80	0.00028	0.0060	0.0058
5.0	0.05	0.0003	2.85	2.75	0.00028	0.0060	0.0056
5.0	0.008	0.0003	3.00	2.90	0.00029	0.0060	0.0058
5.0	0.49	0.0005	4.70	4.60	0.00046	0.0100	0.0092
5.0	0.19	0.0005	4.90	4.80	0.00048	0.0100	0.0096
5.0	0.05	0.0005	4.80	4.70	0.00047	0.0100	0.0094
5.0	0.008	0.0005	4.90	4.80	0.00048	0.0100	0.0096

BRONZE 90:10.

Copper taken.	Arsenic taken.	Antimony added.	No. of c.c. required.		Antimony recovered.	Antimony.	
Grms.	Grm.	Grm.	Total.	Nett.	Grm.	Added. Per Cent.	Found. Per Cent.
4.5	0.5	Blank	0.10	—	—	—	—
4.5	0.5	0.00005	0.60	0.50	0.00005	0.0010	0.0010
4.5	0.5	0.00010	1.1	1.0	0.00010	0.0020	0.0020
4.5	0.5	0.00025	2.4	2.3	0.00023	0.0050	0.0046
4.5	0.5	0.00050	5.0	4.9	0.00049	0.0100	0.0098
4.5	0.5	0.00075	7.4	7.3	0.00073	0.015	0.0146

CUPRO-NICKEL 80:20.

Taken.	Antimony added.	No. of c.c. required.		Antimony recovered.	Antimony.	
Grms.	Grm.	Total.	Nett.	Grm.	Added. Per Cent.	Found. Per Cent.
5.0	Blank	0.40	—	—	—	—
5.0	0.0020	2.5	2.1	0.00021	0.0040	0.0042
5.0	0.0030	3.4	3.0	0.00030	0.0060	0.0060
5.0 (another sample Blank=0.2 c.c.)	0.0050	5.1	4.9	0.00049	0.010	0.0098

BRASS 70:30.

Taken.	Antimony added.	No. of c.c. required.		Antimony recovered.	Antimony.	
Grms.	Grm.	Total.	Nett.	Grm.	Added. Per Cent.	Found. Per Cent.
4.27	Blank	0.1	—	—	—	—
4.60	0.00025	2.4	2.3	0.00023	0.0054	0.0050
4.07	0.0004	4.0	3.9	0.00039	0.0098	0.0096

A point of paramount importance in this process is the acid strength necessary in the quantitative separation of antimony on copper in the presence of cuprous chloride. While it was known from the previous work of Evans that cuprous chloride had no fundamental inhibitive effect on the Reinsch reaction, yet very low results were obtained in the early stages of the work with the acid concentration usually used in the Reinsch test.

This was at first thought to be due to the action of atmospheric oxygen in preventing complete reduction of the copper in solution, but the results were not improved by excluding air and passing a stream of carbon dioxide into the flask during the boiling with copper.

Series of experiments were carried out with progressively increased hydrochloric acid concentration. With 50 c.c. of hydrochloric acid in 300 c.c. of solution at the commencement of the boiling with a copper coil, for example, results were obtained which were low to the extent of about 70 per cent.; the greater the amount of antimony taken, however, the greater was the percentage recovery. Using 150 c.c. of hydrochloric acid (sp. gr. 1.18) in 300 c.c. of solution, quantitative results were obtained. It would seem, therefore, that cuprous chloride renders some hydrochloric acid non-reactive in this connection, probably by withdrawing it into complex combination, so that, unless excess is provided, the amount of effective hydrochloric acid may fall below that necessary for promoting the Reinsch reaction.

Sodium hypophosphite is a most effective reducing agent for use in this process, as a slight excess is sufficient to keep all the copper in the cuprous state during the Reinsch reaction. Nitric acid is somewhat resistant to the reducing action of sodium hypophosphite, so that, if this acid is not removed by fuming with sulphuric acid, a green colour is produced in the solution during boiling, due

to cupric chloride, which is inimical to the quantitative precipitation of antimony. Thorough fuming with sulphuric acid is therefore necessary.

It may be remarked that the process described presents distinct advantage over those described in the two recent Continental papers (Tschernichof, *Z. anal. Chem.*, 1928, 73, 265; Blumenthal, *id.*, 1928, 74, 33). In both these methods the amount of antimony is finally arrived at by titration with *N*/10 potassium bromate solution; as 1 c.c. of this solution is equivalent to approximately 0.003 grm. of antimony, it is evident that a considerable sample weight is necessary when determining the amounts of antimony dealt with in the present paper. These processes were not tested, as it seemed that considerable expenditure of time would be necessary to obtain results of equal accuracy to our own.

Notes.

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

BORIC ACID IN ORANGES.

RECENTLY we had referred to us, by one of the authorities for whom we act as Public Analysts, seven samples of oranges; comprising three Californian, three South African, and one West Indian brand.

These samples were submitted to us because it was believed that oranges were being treated with an antiseptic.

Six of the seven samples were wrapped in papers, in which we found no antiseptic, nor did we find any upon the surface of the peels of any of the samples, but we found that in all the samples the peel and the pulp, which were analysed separately in each case, contained boric acid.

The results obtained were as follows:—

	PEEL.		PULP.	
	H ₂ BO ₃ Per Cent.	Grains per lb.	H ₂ BO ₃ Per Cent.	Grains per lb.
1.	0.033	2.31	0.006	0.42
2.	0.022	1.54	0.002	0.14
3.	0.012	0.84	0.002	0.14
4.	0.008	0.56	0.002	0.14
5.	0.017	1.19	0.004	0.28
6.	0.020	1.40	0.008	0.56
7.	0.005	0.035	0.004	0.28
	Average	1.12		0.28

The average weights of the peel and pulp were 30 and 120 grms. respectively. Samples Nos. 4, 5 and 7 were Californian, Nos. 1, 3, and 6 South African, and No. 2 West Indian; all were wrapped with the exception of No. 7.

Boric acid has before been found to be a natural constituent of oranges, and of a large number of other vegetable substances, in quantities comparable with

those cited above; so that the detection of such quantities of boric acid affords no evidence that it has been purposely added.

The occurrence of boric acid as a widely distributed natural constituent of many food stuffs, animal and vegetable (as well as of the common salt used in their preservation), is of special interest in view of the fact that its use is now prohibited under the Public Health (Preservatives, etc., in Food) Regulations, 1925; and we consider it of sufficient importance to call attention to the matter.

J. T. DUNN.

H. CHARLES L. BLOXAM.

INSTABILITY OF PRECIPITIN ANTI-SERA IN THE TROPICS.

I HAVE read with great interest Mr. Bamford's note on this question (*ANALYST*, October, 1928, p. 531), and believe that it will help to throw light on a difficult problem.

Mr. Bamford suggests bacterial action as the cause of instability. This is a tempting hypothesis, and the first of which one thinks, although in this laboratory it has been found that *all* anti-human precipitin sera (in sealed ampoules) lose their potency in three months.

But is it not significant that many workers (including those in this laboratory) have obtained good reactions with putrid human blood, which must necessarily have undergone bacterial decomposition? It cannot be inferred that bacterially decomposed anti-sera will also react, but good reactions have been obtained in this laboratory from anti-sera which were apparently decomposed. It is, of course, impossible to use such anti-sera for tests to be quoted in the Courts. These considerations have suggested a doubt as to bacterial decomposition being the cause of instability of anti-sera.

Mr. Bamford mentions anti-sera for (apparently) other than the human species which have been proved stable (? albeit weakened), though submitted to variations of temperature (up to 15° C.) for five years. It would be interesting to know if any anti-human sera were included. Is it possible that anti-sera for species other than human are more stable than human anti-sera? Or is the cause of their (apparent) stability the powerful character of the original anti-sera?

Variability in temperature has seemed the only hypothesis left to account for instability of anti-sera. It is, perhaps, possible that anti-sera would lose their potency with comparative rapidity if maintained at the blood temperature of the rabbit or other species used as reservoir. Mr. Bamford mentions various anti-sera which had been subjected to temperatures of 30–35° C. for twelve days before they were tested. At that time they were satisfactory, but for what length of time would they have remained stable?

From a study of the literature and from some experience the picture one has formed of these anti-sera is that of unstable compounds, produced at the blood temperature (probably of the rabbit), which are always tending to revert to their original molecular constitutions, particularly at the temperature of the blood of the rabbit or other animal used for their preparation. Anti-sera made from a bird might possibly be more stable than anti-sera made from a mammal.

The subject is obscure, and all chemists interested in anti-serum tests will welcome contributions thereto.

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(*Government Analyst, Trinidad and
Tobago, B.W.I.*).

THE PRODUCTION OF UNIFORM STAINS IN THE GUTZEIT TEST FOR ARSENIC.

LERRIGO (ANALYST, 1928, 53, 90) has called attention to the occasional difficulty experienced in removing mercuric chloride papers which have been attached with seccotine to the top of the tube of the B.P. 1914 (Appendix VI) apparatus.

I find that tearing of the paper is avoided by the use of "Gloy"; a square (length of side, 18 mm.) of mercuric chloride paper is laid on a clean surface on the table and the rim of the glass tube, previously treated with "Gloy," firmly pressed upon the paper. The attached rubber cork is then re-inserted in the bottle. The paper is afterwards removed with greater ease than would be the case with a disc cut to the exact size of the top of the tube.

Apart from the 20 c.c. tap funnel the apparatus conforms to the requirements laid down in the B.P. 1914 (Appendix VI).

C. H. MANLEY.

AN IMPROVED MISCOMETER.

THE miscometer described in the ANALYST (1926, 51, 453) has been replaced by an alternative form of apparatus. In the new apparatus the measuring device is more

satisfactory, and the measuring chamber has been lengthened and narrowed. The apparatus is simpler to manipulate and is cheaper.

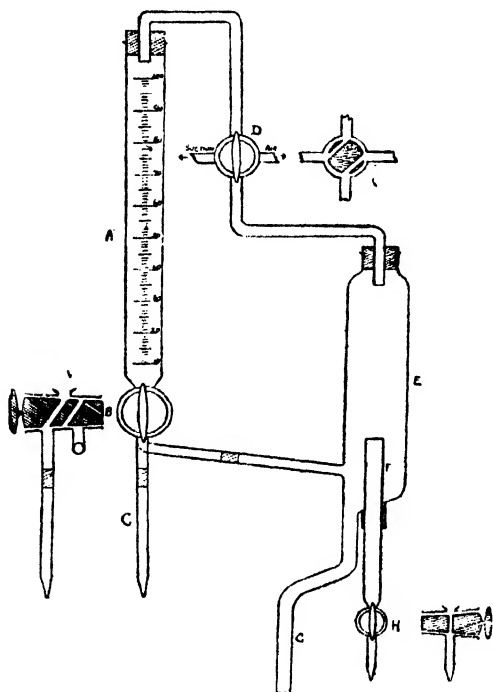
It will be seen from the figure that the new measuring device consists of a burette instead of a hollow stopper. The hollow stopper proved expensive to make and difficult to graduate accurately. The burette may be made quite accurate by grinding down the top to the required dimension. Different burettes may be fitted to deliver quantities of different volumes.

The new miscometer is used in the following manner:—With the suction pump operating and connected with the measuring chamber (A), the samples to be made composite are drawn in turn into the measuring chamber by opening the stopcock (B), which is so left that the inlet tube (C) drains. The samples are mixed by turning the stopcock (B) so that it connects the two chambers. Air is thus drawn through the mixture. When mixing is complete the stopcock (D) is turned through an angle of 90°. The

composite sample is thus drawn into the second chamber (E). During this operation the burette (F) fills up, and at the end of the operation the remainder of the composite sample flows out (by gravity) through the outlet tube (G) into any suitable receptacle. Stopcocks (B) and (D) are then closed, and the measured quantity is drawn off by opening stopcock (H).

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Notes from the Reports of Public Analysts.

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM.

REPORT OF THE CITY ANALYST FOR THE THIRD QUARTER, 1928.

DURING this quarter 1260 samples were analysed, of which 1098 were under the Food and Drugs Acts. Of these, 1024 were bought informally (51 adulterated), and 74 were formal samples (9 adulterated).

CREAM.—The whole of the 18 samples were free from boric acid, but one was composed of artificial cream and the vendor was cautioned. Another was a sample of tinned cream which contained 23 per cent. of fat and was marked: "Pure Thick Cream," "Highly Concentrated." This was a false label, as the sample contained only about half the proportion of fat present in a good "thick" cream.

VERMICELLI.—Four informal samples sold as vermicelli contained from 11.0 to 12.9 per cent. of protein. One sample was described as "——'s Egg Vermicelli," for which there is no standard. The label, however, stated that if four ounces of egg vermicelli were taken to make vermicelli omelet, only one egg would be necessary, instead of two eggs if ordinary vermicelli were used. This was a false label, as it claimed that four ounces of the egg vermicelli were equal to four ounces of vermicelli and an egg. If this had been true, about 100 grains of fat and 300 grains of protein should have been present in that quantity, instead of the 9 grains of fat and 230 grains of protein which were actually present. The vendor was cautioned.

BORAX HONEY.—Five of the 13 informal samples were of incorrect composition; 10 per cent. of borax should be present in this preparation, but in three samples the amounts present were 2.9, 4.4 and 8.2 per cent., respectively.

Two samples from one vendor were labelled "Guaranteed to conform with the requirements of the British Pharmacopoeia," but had been prepared with artificial honey instead of the genuine article. The vendors of the five samples were cautioned.

SODIUM CITRATE TABLETS.—Samples containing two and three grains were of full strength, and broke down very well in water. In each case about 6 per cent. of talc was present. This seems to be an undesirable constituent for tablets which are often used for babies. The manufacturer undertook not to use talc in these tablets in the future.

TINCTURE OF MYRRH.—Eleven of the 13 informal samples varied in specific gravity from 0.851 to 0.864, and contained from 5.3 per cent. to 7.8 per cent. of total solids. Two samples were condemned, as they only contained 4.3 per cent. and 4.2 per cent. of total solids, respectively, and the vendors were cautioned.

The question arose as to whether the low solids in the last two samples were the result of unsatisfactory keeping, and experiments were made on this point. About 2 oz. of tincture of myrrh were kept in a 4 oz. bottle with a narrow neck,

and the bottle was left unclosed for 49 days. At the beginning of the time the total solids amounted to 5.5 per cent., and at the end of that period to 8.7 per cent. The sample remained quite clear, and so it was evident that the only change taking place was concentration due to evaporation of the spirit, and that enough spirit remained to keep the dissolved matter in solution.

The effect of keeping, therefore, was to increase the proportion of solid matter, and not to diminish it.

J. F. LIVERSEEGE.

Legal Notes.

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

ARTIFICIAL VINEGAR: LIABILITY OF RETAILER.

HIGH COURT APPEAL CASE. PRESTON v. JACKSON.

ON November 23 an appeal was heard in the High Court, King's Bench Division, by the Lord Chief Justice, sitting with Mr. Justice Avory and Mr. Justice Acton, against a decision of the Atherstone (Warwickshire) magistrates, not to convict the respondent, a grocer, for selling vinegar not of the nature, substance and quality demanded.

The appellant, an inspector under the Food and Drugs Acts, had asked for "table vinegar," and had been supplied with an article which, on analysis, was found to consist of 100 per cent. of artificial vinegar. The justices, said counsel, seemed to have come to the conclusion that, as there was no standard of quality for vinegar, it was for the prosecution to prove that the respondent had some guilty knowledge when he sold the vinegar. But under section 6 of the Act the question of guilty knowledge did not arise. If goods were sold that contravened the Act an offence had been committed. The respondent was a village grocer, and he had in his shop a cask containing, according to the label, "Finest table vinegar, wholesome." The inspector bought some, and, when analysed, it was found to be artificial.

The Lord Chief Justice asked: "What is artificial vinegar?"

Mr. Bartley replied that it was not vinegar at all, not having been made from cereals and without phosphates.

Mr. Justice Avory: "A synthetic vinegar. Merely diluted acid with a little colour."

Mr. Bartley, continuing, said that there was evidence before the justices that malt vinegar was sold by wholesalers at 8s. 6d. for six gallons, whilst artificial vinegar cost about 4s. for the same quantity. The appellant had been charged for malt vinegar. For the respondent it has been urged that there was no fixed standard for vinegar, and that therefore he had not been guilty of an offence, although he might have sold as "table vinegar" an artificial vinegar that had not been produced by fermentation or acetification, but no evidence had been called for the respondent. The justices had refused to convict, considering that no

question of law arose, and that, if anyone ought to be punished, it should be the wholesalers who sold the liquid to the respondent, and charged 8s. 6d. for stuff that was worth only 4s.

Mr. Justice Avory asked whether these justices were Members of Parliament, since they seemed to think that they could alter the law instead of carrying it out.

Mr. Sandlands, for the respondent, contended that the justices meant to deal with the case under the Probation of Offenders Act, but the Lord Chief Justice pointed out that to have dealt with the case under that Act, the justices must first have found that an offence had been committed. This they had not done. They had found, indeed, that the offence had not been committed by the respondent, for they said: "The inspector went to the shop, asked for table vinegar, and got it, according to the label on the cask." Upon the uncontradicted evidence of the analyst the only course open to the justices was to convict the respondent. Therefore the case would go back to them with an intimation that the only true conclusion in law was that the charge had been proved. The appeal succeeded, with costs.

The other Justices concurred.

PARAFFIN WAX IN DRIPPING.

ON November 16 a firm of manufacturers was charged, at the Birkenhead Police Court, with consigning beef dripping containing paraffin wax to a stallholder in the Birkenhead market, on October 15.

Mr. H. E. Davies, Public Analyst, said that he had analysed a sample of the dripping, and had found it to contain 8.4 per cent. of paraffin wax. He stated that the wax was not only an adulterant, but might set up indigestion in anyone consuming the dripping.

The solicitor for the defence said that the firm had bought the business about 18 months before, and, unfortunately, had carried on the old methods of dealing with the dripping. On making enquiries, they had found that the man responsible for making the dripping used paraffin wax for stiffening purposes.

A director of the company said that they had no knowledge that any harmful adulteration was taking place. The wax had been supplied to them as lard wax; instructions had been given that its use was to be discontinued.

The Chairman of the bench said that it was the duty of manufacturers to make themselves acquainted with the materials they used. A fine of £10 with £1 11s. 6d. costs was imposed.

International Standard Measurements for Mineral Water Analysis.

THE International Society of Medical Hydrology was founded seven years ago by Dr. R. Fortescue Fox, its first President, and still the Chairman of its Council. It is a medical society, having for its chief object the advancement of scientific and systematic conceptions in the use of mineral waters for the treatment of disease and the promotion of health. It is obvious that this object demands as one of its foundation stones some systematic scheme of analysis of the waters

concerned, and with this object in view it appointed, on the occasion of its Annual Meeting in Rome, in October, 1927, an International Standard Measurements Committee to draw up recommendations. This Committee includes:—Professor Chassevant (France), Sir John Flett (England), Dr. Fitch (U.S.A.), Dr. Fresenius (Germany), Dr. S. Judd Lewis (London), Professor Nasini (Italy), Mr. Race (Buxton), Mr. Woodmansey (Harrogate), Dr. Zörkendörfer (Czechoslovakia).

In October this year, the Society held its Annual Meeting in London, and adopted the following resolutions:—

1. That the analysis be expressed in ions, whether it be expressed also in salines or other terms or not.
2. That the quantities be expressed in parts per million; either milligrams per litre or milligrams per kilogram.
3. That the specific gravity refer to water at the same temperature, preferably at 15° or 20° C.
4. That the quantities be limited to four significant figures or to one decimal point, except where the quantity is less than ten, when two decimal figures may be used.
5. That the analysis may be expressed also in terms of salines, the salines being calculated according to an internationally approved arbitrary formula, which has not yet been settled.
6. That the analysis be expressed also in terms of milli-normality ($N/1000$), both in the case of ions and salines.
7. That the analysis, together with other data, be reported according to a definite scheme now under consideration, one feature of which will be that the analytical table will embody four columns:—(a) Name of the ion or saline; (b) proportions in terms of the international standard, namely, parts per million; (c) the same in terms customary in the country where the spring is found; for example, parts per 100,000 in England, grms. per kilogram in Japan; (d) the same in terms of $N/1000$.
8. A National Committee is to be appointed in each country to regularise the publication of analytical and other data.

It should be emphasised that neither the Society nor the Committee has any intention of prescribing methods of determination, except in such cases where uniformity is desirable, as in the specific gravity and the arbitrary formula for calculating salines, and possibly in two or three other cases.

The whole scheme is as yet in embryo, and much has to be done in organising the National Committees, and also in deciding upon a formula for the calculation of the salines from the ions, such as will be generally acceptable by chemists throughout the world, and upon other matters.

It is desirable that all concerned in the analysis and other data relative to mineral springs should keep these resolutions in mind, so that when the scheme is complete, analytical or other information derived in the meantime, may fall into place without difficulty.

S. JUDD LEWIS

(Chairman of the Committee).

Department of Scientific and Industrial Research.

REPORT OF THE FOOD INVESTIGATION BOARD FOR THE YEAR 1927.*

THE Director's Report embodies the results of work done under a very large number of sections, only a few of which can be mentioned.

SECTION A: MEAT.—The transport of chilled beef, conditioning of beef, freezing of tissue, and coagulation of muscles plasma all receive attention. Experiments to determine the best use for surplus pig products of the Dominions suggest that, although bacon cannot be kept for long in the chilled condition, if properly frozen, at a temperature of -10° C. for fresh, and -15° C. for mild-cured bacon, successful results may be obtained.

SECTION B: FRUIT AND VEGETABLES.—Keeping properties of apples may be predicted to a certain extent, since long life is related to low respiratory activity, small size and to small and delayed climacteric. Also, the trees with the largest fruit, as a rule, bear apples with the highest respiratory activity and the shortest life. No marked relation was found between the chemical composition of apples and their keeping properties in cold storage, but bad-keeping apples appear to lose acid and sugar in respiration more rapidly than those that keep better. Oranges stored at various constant temperatures and under two conditions of atmospheric humidity for each temperature, showed two forms of breakdown—a collapse and browning of small scattered areas which was most prevalent at 5° C., and a discoloration of larger areas, with an appearance of water-logged flesh and disagreeable odour, which were more frequent at 1° C. In 60–80 per cent. of the specimens fungal disease developed at the button area of the orange. At temperatures of 25° C., 15° C., and 10° C. damp atmospheres, with 95–98 per cent. relative humidity, on the whole, increased liability to invasion by fungal rot organisms. A study of the water relationships of fruit rotting fungus, particularly of *Alternaria citri*, *Colletotrichum glososporioides*, *Cephalothecium roseum* and *Fusarium fructigenum*, showed that germination could take place in saturated and sub-saturated atmospheres with no other source of water, and the nearer the temperature to the optimum, the lower is the humidity at which germination is possible. The various relationships are illustrated by graphs. Specimens of certain types of wastage of imported fruit have been examined, and a preliminary summary is given in two tables for grape fruits and oranges from different sources, showing the fungi isolated, with remarks on them. In addition, tomatoes from Tenerife and Jersey showed *Phoma destructiva*, *Diplodina lycopersici*, *Pleospora* (*Macrosporia*) sp., and *Fusarium* sp., from rots starting mainly at the stem end; egg fruit from S. Africa, *Alternaria* sp., *Clad sporium herbarum*, *Botrytis cinerea*, and *Macrosporum* sp. (soft spotting); melons from S. Africa *Alternaria* sp. (spotting); peaches from Georgia, U.S.A., *Sclerotinia americana*; and plums from Algeria showed *Rhizopus nigricans*, and from Spain, *Monilia cinerea*.

SECTION C is concerned with large scale storage and transport investigation.

SECTION D: FISH BY-PRODUCTS.—The nutritive value of various fish-meals was investigated on pigs. A comparison between sea bream meal (*Pagellus*

* Obtainable at Adastral House, Kingsway, W.C.2. Price 4s. net.

centrodontus), best white fish meal, and blood-meal and bone-flour, showed that pigs fed on sea bream meal grew faster, and the growth was at the expense of less food. Further, the animals were in better condition, and the curing tests showed that there was not the slightest trace of taint in the flesh. It is shown that the present valuation of fish-meal, which depends on the nitrogen and calcium phosphate content, is not a true criterion of feeding value, and feeding experiments are necessary for evaluation.

Gelatin.—In work on gelatin it is shown that the mode of preparation has a marked effect on its emulsifying power. Treatment with alkalis only is always more efficient, perhaps because the precursor undergoes molecular rearrangement during treatment with acid or alkalis, and the percentage of free amino-groups is greater from an alkali-treated precursor. Thus for electrically purified gelatins the percentages of free amino-nitrogen were:—From calf-skin, SO_2 treated, 3.50, NaOH treated, 4.12; ossein, NaOH, 4.12, HCl, 3.70; fish skin SO_2 , 3.95, NaOH, 4.87; isinglass, 3.75.

The Sterols from the Muscular Tissue of Marine Animals.—The available data on the isolation and identification of sterols from various organisms indicates the presence of very large numbers of isomers of cholesterol of obscure origin, but of biological significance. If derived from plant sterols, the process is complicated. In the case of marine organisms and inferior forms of life the problem is specially complicated, partly owing to the presence of other complex alcohols and sometimes hydrocarbons. Dorée concluded that ordinary cholesterol is obtained from cold-blooded vertebrates and is present as such in invertebrates or as a substitute with similar properties. He showed many points of resemblance between the sterol from *Asterias rubens* and cholesterol, but also that they differed, and later the sterol of *Asterias auranticus* was found to contain a cholesterol isomer. In the present investigation the sterols from cod, skate, octopus, sepia, lobster, oyster, starfish, dogfish, and porpoise brains were extracted by Gardner and Fox's method (*Proc. Roy. Soc.*, 1921, (B), 92, 358); in the case of lobster, oyster and starfish saponification with sodium ethylate was used. The different esters were prepared, fractionally recrystallised, and the properties of the various fractions from which the different isomers were obtained were compared.

It is concluded that two new sterols have been isolated from oysters and starfish, and that the sterol from the muscular tissue of *Octopus vulgaris* is probably different from true cholesterol.

Bleaching of Fish Oils has given satisfactory results on a commercial scale. All free fatty acids are removed by addition of a slight excess of caustic soda, and from the resulting oil emulsion the aqueous alkaline layer may be separated and used for production of cheap soap, whilst the emulsion and any separated oil is washed with boiling water until the wash water comes out colourless; the treatment is continued with a weak solution of sulphurous acid, and after a final water washing the oil is filtered.

Cod muscle protein.—The composition of cod muscle protein was as follows per 100 parts dry protein: Tryptophane 2.2; tyrosine, gravimetric 2.3, colorimetric 3.9; cystine (from S-content) 4.1; leucine 11.7; valine, 3.0; aspartic acid, 4.8; glutamic acid, 7.8; phenylalanine, 1.1 (part only); proline, —; lysine, 7.6; arginine, 11.5; histidine, 1.5; ammonia, 1.3; total, 60.5.

SECTION E is concerned with engineering practice.

SECTION F deals with researches for the Director by the Imperial College of Science and Technology in connection with fruit. In the factors affecting the

Origin.	Kahlenberg (AsCl ₃).	Salkowski-Whitby's modification.		Liebmann-Burchard.	Tschugajeff.	Whitby's Reaction C.
		(a)	(b)			
Cod, m.pt. 144°C.	Cherry red, mauve on boiling, muddy green on cooling	(1) Cherry red (2) Brown, with green fluorescence	Bright blue	Reddish purple	Colourless, pink on heating	Blue
Skate, m.pt. 144°C.	Purple, blue to green on boiling, muddy green on cooling	(1) do. (2) do.	do.	Reddish purple, with green fluorescence	do.	do.
Octopus, m.pt. 146°C.	Pink, remained so on boiling, blue-green on cooling.	(1) do. (2) do.	do.	do.	do.	Colourless
Sepia, m.pt. 147°C.	Pink, purple on boiling	(1) do. (2) do.	do.	Dark rose, with brown tinge	Yellowish pink, intensified on heating	Blue
Lobster, m.pt. 149°C.	Purple, blue-green on boiling	(1) do. (2) do.	do.	Reddish purple, green fluorescence	Colourless, pink on heating	do.
Oyster, m.pt. 116°C.	Reddish brown, dark muddy green on boiling	(1) Pale reddish yellow (2) Yellow red	Colourless	Dark reddish brown	Yellow green, intensified on heating	Greenish-yellow
Starfish, m.pt. 142°C.	Light brown, dark muddy-green on boiling	(1) Pale yellow (2) Yellow red	Pale yellow	Dark amber	Yellow green, intensified on heating, with blue fluorescence	Reddish-brown
Dog-fish brain, m.pt. 146°C.	Purple, blue-green on boiling, muddy-green on cooling	(1) Cherry red (2) Brown with green fluorescence	Bright blue	Reddish purple, green fluorescence	Colourless, pink on heating	Blue
Porpoise brain, m.pt. 146°C.	Cherry red, intensified on boiling	(1) do. (2) do.	do.	do.	do.	do.

internal resistance of apples to fungal disease it was found that: (a) Each individual apple in a sample has a characteristic resistance; (b) the rate of invasion in an apple of a given variety does not remain constant, but may rise or fall in time according to the variety used and the experimental conditions; (c) a comparison of *Fusarium* strains on various apples has shown that the virulence of the strains falls into an order which is independent of the variety of apple and the seasonal changes, but is affected by the temperature of storage. All the saltants examined exhibited a lower virulence than the original strains from which they were derived; (d) locality of origin influences resistance and differences can be correlated with differences in chemical composition; (e) resistance is complex, as *e.g.* low water content, high acidity and potash content and low nitrogen content are associated with high resistance and *vice-versa*.

SECTION G: INVESTIGATION OF SQUALENE.—Researches conducted by the University of Liverpool include an investigation into squalene. The formation of squalene can be regarded as the result of "head and tail" linking of 6 isoprene nuclei. It is probably synthesised in the living organism by aldol condensation of the aliphatic plant terpene aldehydes such as citral, citronellal or farnesal, followed by reduction in the animal liver. The formula of batyl alcohol is given as $C_{21}H_{44}O_3$; it is a saturated dihydric alcohol characterised by means of its phenylurethane and *p*-nitrobenzoate. The higher fatty alcohols found in many Elasmobranch fish are definitely related to those found in sperm-whale oil, for octadecyl, oleyl and cetyl alcohols, occurring in the latter, are present in the liver oils combined with glycerol, and selachyl and chimyl alcohols are also found. The occurrence of these glycerides in nature, forming a link between the fats and waxes, is of outstanding biological interest, and they are probably common constituents of other fish oils. They have no direct connection with vitamin A.

Cholesterol and Vitamin D.—The work on cholesterol and vitamin D has given fairly definite evidence that vitamin D is related to an absorption band with maximum at 247μ , and a detailed spectrographic examination of various cholesterol derivatives proves that selective absorption is only shown when at least 2 ethenoid linkages are present in the sterol molecule. The absorption spectrum of cholesterol bears a close resemblance to that given by the pro-vitamin, and it is probable that of the 3 double bonds in ergosterol, 2 occupy the same positions as in cholesterol. The absorption spectrum of cholesterol shows 2 bands at 312 and 242μ , the latter being very similar to the vitamin D band at 247μ . The passage of cholesterol to a cholesterolone is the fundamental reaction taking place whenever the former is decomposed by heat.

D. G. H.

Standard Method of Prussiate Analysis.*

IN the modern practice of buying chemical products on the analytical basis it is necessary that some particular and standardised method should be agreed upon between buyer and seller which is to be used in case of dispute. This has been done long since in most branches of the industry, but there are still some chemical products on which no general agreement has been reached.

* At a recent meeting of the prussiate makers of the world a standard method of analysis was agreed upon, and it was arranged that this standard method of analysis should be published in the various countries by the different workers. The method has been submitted to the *ANALYST* as one of the two journals for the English communication.—EDITOR.

In the prussiate industry a number of analytical methods, more or less accurate and convenient, are recognised. Some of these methods, while accurate for the estimation of pure ferrocyanides, are unreliable when used on the commercial product, because of the possible presence of certain impurities which render the method inaccurate; unless special precautions are taken to eliminate or render them inoperative.

Until quite recently no attempts have been made to judge of the merits of the various analytical methods for the estimation of ferrocyanides from the point of view of its use for the analysis of the commercial article and not of the chemically pure product.

For this purpose the method selected should be both accurate and rapid. It must not be influenced by any impurity likely to be present in the commercial article, and it should not require a very high order of skill or practice.

The various methods of ferrocyanide analysis in general use may be roughly classed under the following heads:

1. Conversion into hydrocyanic acid and estimation as sodium cyanide by standard silver nitrate solution.
2. Oxidation methods.
4. Titration with a salt of a heavy metal or other body capable of forming an insoluble ferrocyanide.

Under the first head the cyanogen of the ferrocyanide is distilled off as hydrocyanic acid either by the method of W. Feld (*J. Soc. Chem. Ind.*, 1903, 1068), in which the ferrocyanogen radicle is broken up by boiling with mercuric chloride and the cyanogen converted into mercuric cyanide, which is then distilled with an acid; or by the method of H. E. Williams (*J. Soc. Chem. Ind.*, 1912, 315), in which the ferrocyanide and acid is distilled with a small quantity of cuprous chloride, the latter acting catalytically in breaking up the ferrocyanide and converting the cyanogen contents into hydrocyanic acid.

The hydrocyanic acid evolved is absorbed into dilute caustic soda solution, and the resulting cyanide solution titrated with standard silver nitrate solution after the addition of a few drops of a 10 per cent. solution of potassium iodide.

Both these methods are accurate if performed with care, but the results are liable to be somewhat low, particularly the former, owing to the fact that slight losses may occur in the different operations, which are accumulative and appreciable when estimating material for 100 per cent. purity.

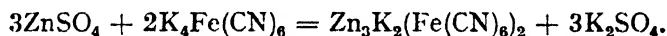
They have the advantage that the cyanogen content is finally titrated by a solution which may be accurately standardised by known and accepted methods, instead of by standardisation with what may or may not be pure ferrocyanide. On the other hand, while the cuprous chloride method is comparatively simple, both methods require considerable skill and practice, and are therefore not suitable for general analytical practice.

Under the second heading, titration of the ferrocyanide solution with a standard solution of potassium permanganate is the most general method, and the only one that need be considered here. The method is simple, the standard solution of permanganate is generally found in any analytical laboratory, and it is easy to standardise. Unfortunately, however, the method is liable to very considerable inaccuracy, owing to the possible presence in the ferrocyanide of oxidisable impurities, both organic and inorganic, which render the results obtained much higher than the truth. The oxidisable impurities likely to be present are sulphides, thiosulphates, thiocyanates, organic matter, and in the case of synthetic ferrocyanides, formates. This method, therefore, should not be used for the estimation of commercial ferrocyanides.

In the third class of methods, the ferrocyanide solution is exactly precipitated with a solution of a heavy metal salt which has been standardised under exactly similar conditions with a solution of a known weight of pure ferrocyanide. A number of metallic salts have been recommended for this purpose, including the soluble salts of copper, nickel, lead, iron, zinc, etc. Of these, only solutions of copper and zinc have come into general practice. When a solution of a copper salt is added to an acidified solution of the ferrocyanide, cupric ferrocyanides are precipitated which vary in composition according to the conditions of the precipitation and the amount and nature of the alkali salts present. Errors also arise if sulphides, thiosulphates, thiocyanates, etc., are present with the ferrocyanide.

These objections to the use of a solution of a copper salt for the titration of ferrocyanides, however, do not apply to the use of zinc sulphate. With this salt the composition of the zinc ferrocyanide is constant, and the impurities likely to be associated with the ferrocyanide have no effect on the composition of the precipitate or the amount of zinc used. Thus sulphides, thiosulphates, thiocyanates, or formates have no effect on the titration.

The main objection against these methods of titration is that the metallic salt solution is standardised against a ferrocyanide which may or may not be pure and dry. When zinc sulphate is used as the precipitating agent this objection has been overcome by the writer, who has found that the composition of the precipitate under the conditions of the titration when potassium ferrocyanide is used is constant and agrees with the formula $\text{Zn}_3\text{K}_2(\text{Fe}(\text{CN})_6)_2$. The zinc sulphate solution, therefore, may be made up, its zinc contents estimated, and the precipitating equivalent of potassium ferrocyanide for each c.c. calculated, or the solution adjusted until 1 c.c. will precipitate 0.01 grms. or 0.05 grms. as desired, of potassium ferrocyanide, according to the equation:



The standardisation of the solution is thus independent of a ferrocyanide.

When sodium ferrocyanide is precipitated by a soluble zinc salt, the composition of the precipitate closely approximates to the formula: $\text{Zn}_3\text{Na}_2(\text{Fe}(\text{CN})_6)_2$. But if potassium chloride solution is added (20 c.c. of 20 per cent. solution) before titration, a precipitate of constant composition is obtained, agreeing with the formula: $\text{Zn}_3\text{K}_2(\text{Fe}(\text{CN})_6)_2$, so that either potassium or sodium ferrocyanide may be titrated with equal accuracy, provided that in the case of the latter salt a solution of potassium chloride or sulphate is added before titration.

For the analysis of commercially pure sodium ferrocyanide, the zinc sulphate solution may, if preferred, be standardised with chemically pure sodium ferrocyanide.

The determination of the impurities of a ferrocyanide is sometimes a question of importance, and the usual laboratory methods cannot be applied without a preliminary treatment. The impurities that may possibly be met with in ferrocyanide are chloride, sulphate, thiosulphate, thiocyanate, formate, carbonate, cyanide, mechanical impurities in the form of insoluble dirt and dust, etc.

Below is given an outline of methods for the estimation of the most probable and important impurities of ferrocyanides worked out by the writer.

Take 50 grms. of the ferrocyanide, dissolve in about 250–300 c.c. of distilled water and precipitate with a slight excess of pure recrystallised zinc acetate, dilute to 1000 c.c., shake well and filter.

Determination of Chloride.—Take 100 c.c. of the clear filtrate in a 300 c.c. beaker, add a few drops of potassium chromate solution, and titrate with *N*/10

or $N/100$ silver nitrate solution in the usual manner. The end-point is sharp and distinct.

Determination of Sulphate.—Acidify 100 c.c. of the clear filtrate with pure hydrochloric acid, boil, and then add an excess of boiling barium chloride solution, filter, ignite, and weigh as barium sulphate.

Determination of Formate.—Take 100 c.c. of the clear filtrate, add an excess of mercuric chloride solution together with a few drops of acetic acid, boil for half-an-hour, filter on a tared filter paper, wash, dry and weigh.

Weight of $\text{HgCl}_2 \times 0.178 \times 10 \times 2 = \text{KHCO}_2$ per cent.

Weight of $\text{HgCl}_2 \times 0.144 \times 10 \times 2 = \text{NaHCO}_2$ per cent.

At a recent conference of the chemists of the European Prussiate Manufacturers, the various methods of ferrocyanic estimation were critically examined, and the zinc sulphate titration method finally accepted by them as the standard method of ferrocyanide estimation for the settlement of disputes between manufacturer and customer.

A translation of the findings and the method as agreed to by the chemists of the European Prussiate manufacturers is as follows:

1. It was generally agreed that the permanganate method could not be used, as the presence of oxidisable impurities would give false results.
2. The method for the determination of ferrocyanide by distilling as hydrocyanic acid was agreed by all to be good. Doubts were raised against this method, however, as lower results were frequently obtained by it than by other methods, and it did not seem practicable to accept it as a general standard method which was to be made available for public laboratories. The method in which mercuric chloride was used was preferred to that in which cuprous chloride was used.
3. The copper sulphate method was generally condemned, as it had been found that the results were not reliable, variable compounds being readily formed.
4. The copper sulphate method of converting the ferrocyanides into ferricyanides was agreed to be good so long as no sulphur compounds were present. Sulphur compounds caused the precipitation of copper, so that for this reason the method was unreliable under certain conditions.
5. The zinc sulphate method was agreed by all to be the best method.

METHOD OF PROCEDURE.

STRENGTH OF SOLUTIONS.

Zinc Sulphate Solution.—About $1/5$ th normal solution (28.7 grms. to a litre) is standardised against Kahlbaum's potassium ferrocyanide and the factor thus determined.

Ferrocyanide Solution.—Ten grms. of the ferrocyanide are dissolved in water, and the solution diluted to 500 c.c. Fifty c.c. of this solution are taken for analysis. They are diluted with water, and acidified slightly with dilute sulphuric acid (about 10 c.c. of $1/10$ th normal pure (iron free) sulphuric acid). A 15 per cent. solution of pure iron alum is used as indicator. Titration is carried out at a temperature of $15-20^\circ \text{C}$. The paper used for the determination of the end of the titration must be iron-free and, in particular, as ash-free as possible. The

titration is carried out by adding the zinc sulphate solution to the acidified potassium ferrocyanide solution. The end-point is determined by placing 2-3 drops of the titrated solution on a filter paper by means of a glass rod and leaving the paper for a few minutes to let the drops spread well. Then one or more drops of the indicator solution are placed on the paper at a distance of 1-1½ cm. The end of the titration is shown when no trace of the blue colour appears at the junction of the two liquids. Special care must be taken to see whether any blue colour appears about 2-3 minutes after the two liquids come into contact. It is best, when placing the drops on the paper, to make a dent in it with the glass rod, as by this means the precipitate is kept back more easily and not carried to the outside edge. It is necessary to do this, for a blue colour will always appear when the iron salt comes into contact with the precipitated zinc ferrocyanide.

If such a quantity of the liquid to be titrated is taken for the drop tests that it considerably influences the final result, the titration must be repeated, and the zinc sulphate solution allowed to flow into the liquid to be titrated until just before the termination with a minimum of drop reaction tests, *i.e.* with a minimum loss of solution. It may be stated here that a drop taken on a thin glass rod represents about 1/10th c.c. of the titration solution.

MOISTURE.—A determination of the moisture contents should follow. This is determined by placing a weighed quantity in a drying oven at a temperature of 125° C. to drive off the moisture and water of crystallisation, until constant weight is obtained. The moisture content is calculated by subtracting the calculated water of crystallisation from the difference between the original weight taken and the dry weight.

SAMPLING.—As a special method of sampling it is recommended that a sample should be taken from each cask, so that for each ton of goods a kilo. sample is taken. This sample is to be divided into four containers and sealed. The sampling is to be done by a sworn sampler from the Chamber of Commerce or a similar authority.

Parliamentary Notes.

EXPIRING LAWS CONTINUANCE ACT, 1928.

THIS Act continues—"So far as it authorises the making or revoking in whole or in part, of Part III of the Sale of Food Order, 1921, and provides for the enforcement and imposes penalties for the breach thereof."*

* Part III, Sale of Food Order, 1921, deals with the labelling of certain imported produce.—
EDITOR.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

New Carbohydrate in Rye Flour and Detection of Rye Flour in Wheat and other Flours. J. Tillmans. (*Z. Unters. Lebensm.*, 1928, 56, 26-32.)—Trifructosan or trifructose anhydride, $C_{18}H_{30}O_{15}$, is a new carbohydrate isolated from rye flour, and may be identical with the secalose of Schulze and Frankfurt (*Ber.*, 1894, 27, 626, 3525). When pure, it is a white, crystalline, slightly sweet powder, soluble in dilute acids, but insoluble in strong alcohol, optical rotation at $20^{\circ}C.$, -43.93° (-92.70° after inversion). Since it is found only in rye flour, the presence of 10 per cent. or more in wheat or other flours may be detected. The sample (5 grms.) is centrifuged with 20 c.c. of 70 per cent. alcohol for 15 minutes, the mixture maintained at $-3^{\circ}C.$ for 10 minutes, then well stirred, and again centrifuged for 5 minutes. The extract is decanted, filtered clear if necessary, and 10 c.c. added to 0.5 c.c. of a *N* solution of sodium hydroxide in 70 per cent. alcohol. Pure wheat flour yields, at the most, a white turbidity, but if rye flour is present, a distinct precipitate of the sodium salt of trifructosan is produced. J. G.

Determination of Reducing Sugars, especially Dextrose, in Presence of Hydrocyanic Acid by means of Alkaline Copper Solutions. H. Hérissé and A. Chalmers. (*J. Pharm. Chim.*, 1928, 8, 393-406.)—When applied to the determination of dextrose in presence of hydrocyanic acid, Bertrand's method gives low results, the precipitation of cuprous oxide being lessened or, sometimes, prevented entirely owing (1) to the interaction of the sugar and hydrocyanic acid, according to Kiliani's reaction, (2) to precipitation of cuprous cyanide, and (3) to solution of the cuprous oxide by the hydrocyanic acid. On the other hand, sensibly exact results are obtained by a volumetric method in which the end of the reaction is judged by the decolorisation of the alkaline copper solution. Hydrocyanic acid may be eliminated from pure sugar solutions by evaporating the liquid to dryness. When the products of the enzymic hydrolysis of amygdalin are to be tested, the effect of the hydrocyanic acid may be overcome by evaporating 20 c.c. of the solution to 10 c.c. on a boiling water-bath, shaking with 1 c.c. of lead acetate solution and 2 c.c. of saturated sodium sulphate solution, making up to 30 c.c. with water, again shaking and filtering. The hydrocyanic acid may be eliminated also by subjecting the solution to the prolonged action of a current of air, or by precipitating with silver nitrate, excess of this being removed by precipitation with sodium chloride. T. H. P.

Detection and Determination of Sucrose by the Ammonium Molybdate Method. N. W. Matthews. (*Chemist Analyst*, 1928, 17, 8.)—Solutions of sucrose of the order of 1 in 1000 to 1 in 40,000 may be determined by the addition to 5 c.c. of sample of 3 drops of concentrated hydrochloric acid and 3 c.c. of a 4 per cent.

solution of ammonium molybdate. The mixture is heated in boiling water for 6 minutes, and the blue colour produced is matched against that of a suitable standard prepared under the same conditions. The standards, which are not permanent, may be substituted by Fehling's solution or blue-black ink, suitably diluted.

J. G.

Iodine Value of Spanish Paprika Oil. L. C. Mitchell and S. Alfend. (*J. Assoc. Off. Agric. Chem.*, 1928, **11**, 523-527.)—Eleven authentic samples of paprika pods, grown in various districts in Spain in 1927, were separated into shells, seeds, and placentae, these being dried and, as is the commercial practice, mixed in varying proportions according to the grade or quality required, and ground. The procedure adopted in the extraction of the oil and in the determination of its iodine value was as follows: To 10 grms. of the ground sample, in a 200 c.c. stoppered flask, were added 100 c.c. of chloroform, the flask being rotated during the introduction of the first 50 c.c. After being left for an hour, the flask was shaken and the contents filtered through a 12.5 cm. fluted filter. From 10 c.c. of the filtrate, the solvent was evaporated in a weighed crystallising dish, 50 × 35 mm., which was afterwards kept at 100° C. for an hour, cooled in the air, and weighed. Another 10 c.c. portion was treated, in a suitable glass-stoppered flask or bottle, with 30 c.c. of Hanus solution, and the iodine value determined by the official method of the Assoc. Off. Agric. Chem. (*Methods of Analysis*, 1925, p. 287).

The limiting (and average) numbers obtained for the iodine values are: For mixtures containing shells (53.9-60.8 per cent.), seeds (34.6-41.9 per cent.), and placentae (4.0-8.8 per cent.) in their natural proportions, 134.0-138.9 (136.5); for mixtures containing 70 per cent. of shells and 30 per cent. of seeds and placentae, 133.6-139.7 (136.5); and for mixtures containing 45 per cent. of shells and 55 per cent. of seeds and placentae, 133.0-136.4 (134.5). Thus, the lowest iodine values were obtained in the series containing the largest proportion of seeds and, therefore, of oil. The range of iodine values specified by the official U.S. Standards, namely, 125-136, is not applicable to the results obtained by the chloroform extraction method.

T. H. P.

Crab Liver Oil. M. Tsujimoto. (*J. Soc. Chem. Ind., Japan*), 1928, **31**, 279B.)—The liver oil of the Japanese crab, "Tarabakani" (*Paralithodes Camtsehatica*, Tilesius), is a dark brown liquid with a characteristic and unpleasant smell. The colour reaction with sulphuric acid is slightly greenish dirty brown. On saponification a brownish-red precipitate is formed which contains nitrogen and sulphur. The sample examined had the following constants:—Sp. gr. at 15°/4°, 0.9456; acid value, 97.9; saponification value, 155.6; iodine value, 163.6; n_D^{25} , about 1.475, and unsaponifiable matter, 6.39 per cent. *Fatty acids*.—M.pt., below 15° C.; neutralisation value, 185.5; iodine value, 183.3; bromides insoluble in petroleum spirit, 116.7 per cent.; insoluble in ether, 56.7 per cent.; bromine content of bromides, 71.5 per cent.; liquid fatty acids, 85.6 per cent.; unsaturated acids, 33.6 per cent.

The iodine value of the unsaturated acids was 320.9. The fatty acids consist

mainly of C_{18} , C_{20} and C_{22} acids. The unsaponifiable matter is viscous and orange in colour, dissolving readily in methyl alcohol (hydrocarbons absent). With acetic anhydride and sulphuric acid the colour is violet red, changing to bluish and finally dark green. With antimony chloride in chloroform there is no remarkable coloration, indicating the possible absence of vitamin. The unsaponifiable matter contains 22.67 per cent. of cholesterol, also batyl, selachyl and possibly chimyl alcohols. The authors also report the presence of a new unsaturated liquid alcohol with a formula probably of $C_{11}H_{20}O_2$, of which the acetyl derivative distilled below 200° (5 mm.); after hydrogenation the product ($C_{11}H_{22}O_2$) remains liquid at 0° .

R. F. I.

Purity of Ether for Analytical Use. G. Middleton. (*Quart. J. Pharm.*, 1928, 1, 319-326.)—Commercial ether may contain impurities, and the most reactive of these is ethoxyethyl hydrogen peroxide, although other substances, such as aldehyde or alcohol, also exert deleterious effects. Acetaldehyde and the organic peroxide are found in ether stored under unfavourable conditions, especially if the ether is initially impure, and numerous examples are cited in ordinary analytical procedure where the ether has introduced a considerable factor of error. If old ether is used for extraction of a substance subsequently recovered by evaporation of the ether, the residue attains constant weight very slowly, the final weight being higher than if pure ether had been used, and the residue is chemically altered, as shown by a difference in appearance, solubility, iodine value and titration.

D. G. H.

Determination of Iodine in Organic Combinations, especially in Thyroid Gland. W. Smith. (*Quart. J. Pharm.*, 1928, 1, 372-377.)—Many methods for determining iodine in organic combination are criticised and the following adopted. If the iodine content of the material to be analysed is fairly high (about 0.2 per cent.) Hunter's method is used (*J. Biol. Chem.*, 1910, 1, 321), whereby the substance is fused with sodium and potassium carbonates and potassium nitrate, the melt dissolved in water, and the iodide oxidised to iodate in phosphoric acid solution by a slight excess of sodium hypochlorite solution. Excess chlorine is boiled off, the removal being controlled by starch iodide paper until no reaction occurs, and boiling is then continued for 15 minutes. Potassium iodide is then added, and the iodine titrated with 0.005 *N* thiosulphate solution. This method, very slightly modified, is that of the U.S.P. (X.) for the assay of iodine in thyroid gland. For small quantities of iodine a modification of Kendall's method is used, whereby 1 grm. of material is gently heated with powdered sodium hydroxide in a nickel crucible, practically covered, and subsequently the heating increased until the organic matter is oxidised. After being extracted with water and filtered through cotton wool, the mixture is neutralised with syrupy phosphoric acid (bromphenol blue as indicator), excess bromine added, followed by excess of 2 c.c. phosphoric acid. After boiling to half the volume the remaining traces of bromine are eliminated by addition of salicylic acid, and the iodine is titrated with 0.005 *N* thiosulphate solution.

D. G. H.

Determination of Camphor in Pharmaceutical Preparations. J. Bougault and Bl. Leroy. (*Ann. Falsific.*, 1928, **21**, 456-460.)—To 0.5 gm. of camphor, dissolved in 5 c.c. of 90 per cent. alcohol, are added 1 gm. of hydroxylamine hydrochloride in 5 c.c. of water and 2 c.c. of 20 per cent. sodium hydroxide solution, and the tube sealed and placed for 2 hours in a boiling water bath. After cooling, the contents of the tube are washed out with 10 times diluted sodium hydroxide, and 20 c.c. of water added, when a cloudiness forms, due to precipitation of part of the camphoroxime. The cloudiness is redissolved by the addition of 3 c.c. of sodium hydroxide solution, but if it still persists is due to camphene or borneol, which are filtered off. The liquid is exactly neutralised with hydrochloric acid, and the camphoroxime removed by 20 c.c. of ether; the ethereal solution is washed with 5 c.c. of water and decanted into a weighed dish of 7 cm. diameter, and the aqueous solution again extracted with three further portions of ether. The solution is left to evaporate in the air for 12 hours, and the residue dried for 12 hours over calcium chloride and weighed, 4 per cent. being added to the result to compensate for evaporation of camphoroxime. Then the weight of camphor in the sample is given by multiplying the result by 152 and dividing by 167, the molecular weights, respectively, of camphor and camphoroxime. This method may be applied directly to the determination of camphors in tinctures; for camphorated oils the camphor must be separated from the oil, by distilling slowly for 2 hours a mixture of 50 c.c. of water to 20 grms. of camphorated oil, with fragments of pumice in the presence of 30 c.c. of 95 per cent. alcohol added from a dropping funnel, and the distillate is made up to 100 c.c. Synthetic camphor may contain camphene, borneol or isofenchone, but that produced in France rivals the best Japanese camphor in purity.

D. G. H.

Compound Tincture of Benzoin. T. T. Cocking. (*Quart. J. Pharm.*, 1928, **1**, 337-346.)—The complete analysis or evaluation of compound tincture of benzoin requires the determination of total solids, acid, ester, and saponification values, and free, combined, and total balsamic acids. The total solids are found by drying *in vacuo* over sulphuric acid at laboratory temperature. For the acid value 20 c.c. of the tincture are diluted with 50 c.c. of neutral alcohol and titrated with *N* alcoholic potash, and the ester determined in the neutralised liquid. Free balsamic acids are determined in 20 c.c. of tincture in which 2 grms. of light magnesium oxide have been diffused, 100 c.c. of water and 20 c.c. of xylene added, and the whole boiled for 1 hour. After filtering, the separated liquid is boiled again with 100 c.c. of water, separated, and after a third boiling, the combined liquids are washed once with ether. The balsamic acids are then liberated by hydrochloric acid, extracted with ether, which is evaporated, and, after drying, weighed. The total balsamic acids are found by saponification, evaporation, solution of the residue in water, acidification, addition of magnesia and xylene, separation of the aqueous liquid after boiling as before, and weighing of the acids. Tables are given showing the maximum variations in compound tinctures of benzoin, together with figures for commercial samples.

D. G. H.

Microchemical Reactions of Homatropine. M. Wagenaar. (*Pharm. Weekblad*, 1928, **65**, 1213-1216.)—Homatropine, $C_{16}H_{21}NO_3$, a very strong base, crystallises in colourless, hygroscopic, *d*-rotatory prisms (m.pt. 98° C., refractive index 1.56-1.62), which are insoluble in water, easily soluble in alcohol or chloroform, and partly soluble in ether or benzene. Solutions of the strengths indicated give characteristic crystalline precipitates, which may be recrystallised from alcohol, with solutions of gold chloride, picrolonic and picric acids (1 : 250), 0.1 *N* iodine solution (1 : 500), and with Eder's reagent (a solution of 1 part of bromine, and 2 parts of potassium bromide in 20 parts of water) (1 : 1000). The iodine and Eder reagents are unaffected by mineral acids and yield feathery and block-shaped crystals, respectively. J. G.

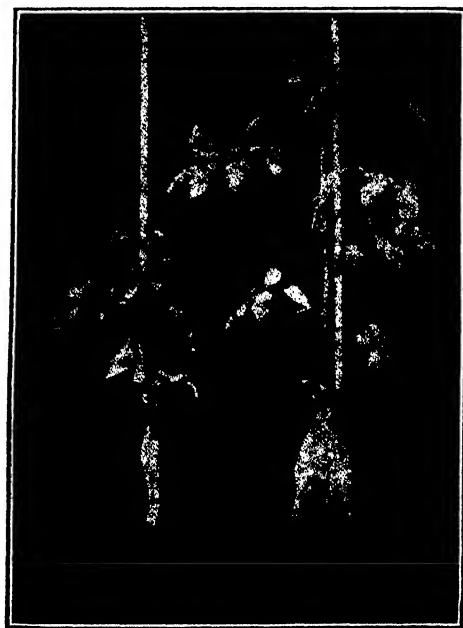
Formula for Calculating Composition of Mixtures of Mydriatic Alkaloids. J. C. Munch and G. S. Gittinger. (*J. Assoc. Off. Agric. Chem.*, 1928, **11**, 521-523.)—Examination of a number of solutions containing atropine mixed with either hyoscyamine, or cocaine, or homatropine, shows that the resultant physiological effect of each such solution is equal to the summation of the separate physiological effects of the two constituents. If, therefore, the concentration necessary to cause just perceptible mydriosis in the cat's eye (threshold value) is known for each of the two alkaloids present and for any given solution containing both, a simple calculation gives the proportions of the two in this solution. T. H. P.

Biochemical.

Note on Quantitative Methods of Measurement of the Nutritive Value of Proteins. H. H. Mitchell. (*Biochem. J.*, 1928, **22**, 1323-1326.)—In a study of the nutritive value of the protein tuberin, Kon (*Biochem. J.*, 1928, **22**, 261) has compared the method of the author (*J. Biol. Chem.*, 1924, **58**, 873) with that devised by Osborne, Mendel and Ferry (*J. Biol. Chem.*, 1919, **37**, 223). The author takes exception to Kon's statement that : " A specific error seems to be inherent in the method . . . namely, the tendency to give higher biological values in the periods immediately following the standardising nitrogen-free or low-nitrogen periods . . .," and to his explanation of the differences in the nutritive ratings of proteins as obtained by the two methods. In the first method, the nutritive value of the protein is taken as the total nitrogen retention of the experimental animal in percentage of the total absorbed nitrogen ; this percentage is called the " biological value " of the protein, a term introduced by Thomas (*Arch. anat. Physiol.*, 1909, **219**) ; in the second method the nutritive value of the protein is measured by the gain in body-weight of the experimental animal per grm. of protein consumed. With regard to the first point at issue, the author states that the question is a statistical one, and cannot be settled by citing isolated instances in which experimental data *appear* to indicate an increased biological value following nitrogen underfeeding. He gives a table which summarises all published data on the effect of a period of low-nitrogen feeding on the biological value of protein obtained in an

immediately following period, and states that as the method is applied in the author's laboratory, there seems no reason to believe that a period of low-nitrogen feeding exerts any but anything inappreciable effect upon the utilisation of protein in a subsequent period. Regarding the differences in nutritive ratings of proteins, he states that the biological value of a protein measures that fraction of the absorbed protein nitrogen that is being used in all of the anabolic reactions of the body, whilst the other method takes notice only of that fraction of protein intake that is being used for growth, so that this latter method of protein value is subject to variation caused by variable food intakes, *i.e.* there is no reference to size of animals used, or to amounts of food consumed. "It is a hazardous undertaking to compare gains per grm. of protein consumed obtained in different experiments without reference to the size of animals employed, or to the amounts of food consumed, as Kon and others before him have done." Differences in sex of rats and digestibility of proteins also affect the results of the numerical method of Osborne, Mendel and Ferry. The author concludes with the statement that the methods are not equivalent, and the results obtained need not parallel each other.

P. H. P.



(a) Tomato plant grown without boric acid.
(b) " " " " with boric acid.

Importance of Boron in Plant Growth. E. S. Johnston. (*J. Chem. Educ.*, 1928, 5, 1235-1242.)—The addition of 0.55 parts per million of boron compounds, expressed as boron, to the nutrient solution in which tomato plants were being grown restored growth, which had been very feeble, to a normal state, and

it was found that the addition of similar quantities of boron to potato plants grown without it greatly improved top growth and doubled the weight of tubers. It was found that potato plants grown in new glazed earthenware jars were able for some time to obtain sufficient boron from the glaze, and similarly tap water proved a sufficient source of supply for tobacco plants. Analytical data of tomato plants grown with and without boron, as percentages of total dry matter per stem and leaves are as follows :—

		Leaves.		Stems.	
Amount of boron added to the nutrient solution (p.p.m.)	..	0.00	0.55	0.00	0.55
Starch	12.03	8.41	5.42	1.45
Reducing sugars (hexoses)	..	8.18	3.83	5.32	8.70
Sucrose	3.31	1.34	3.13	2.89
Total sugars	11.50	5.16	8.45	11.59

A deficiency of boron affects the growing point (and thus the general growth direction) and meristematic tissues, and the conducting system breaks down. This is confirmed by both microscopical and chemical examination. Starch and total sugars are more abundant in leaves of boron-deficient plants than in normal plants, owing to the plants being able to manufacture these substances, but not to distribute them. In boron-deficient potato plants the leaves became thick and rolled, as in potato leaf-roll disease, and starch was abundantly present, as when phloem necrosis occurs. Addition of as little as 0.5 p.p.m. to the nutrient solution corrects deficiencies, but a concentration of only 5 p.p.m. is extremely toxic. Boron should be added to the list of elements necessary for plant growth.

D. G. H.

Valuation of Insecticides. C. H. Peet. (*Ind. Eng. Chem.*, 1928, 20, 1104–1165.)—Many variables have to be considered in testing insecticides biologically; of these, temperature, time, concentration, and humidity may be controlled, but other variables, such as degree of agitation of the air in the chamber and condition of the insect, are more difficult to regulate. For use in experimental work, the author breeds flies (*Musca domestica*) in quantity; although less robust than wild flies, they are of fairly uniform strength, and the age of each batch is, of course, known definitely. Repeated tests have to be made before any definite conclusion as to the efficiency of an insecticide is obtained, and the immediate result of a test is not necessarily the final one. Certain compounds have almost no effect when first applied, but produce high mortality after a longer period of contact; others produce almost instantaneous narcosis from which the insects recover completely after some time.

W. P. S.

Use of Piperazine in the Analysis of Urine and Blood. R. Gros. (*J. Pharm. Chim.*, 1928, 120, 313–316.)—In analysing urines for xanthic bodies and uric acid by the Haycraft-Denigès method 100 c.c. of the well mixed sample are made up to 110 c.c. with an aqueous 10 per cent. solution of piperazine and shaken till clear, and 25 c.c. of Denigès' solution A added. After filtration through a folded filter 108 c.c. are collected, and the original procedure followed. The

addition of the piperazine introduced no source of error, and gave a clear solution where an abundant deposit of uric acid or urates was originally present. In the determination of uric acid in blood by Grigaut's method (modification of the methods of Folin and Wu) the solution of the uric acid in the presence of the mixture of mono and disodium phosphates, may be rapidly brought about by the addition of 10 c.c. of an aqueous 10 per cent. solution of the piperazine. D. G. H.

Glucose in Normal Urine. A. Hassan. (*Biochem. J.*, 1928, 22, 1332-1340.)—A trustworthy method is described for the preparation of the osazones of the urine sugars. The urine is treated with adsorbent charcoal before application of the phenylhydrazine test; in this way the substances in urine which interfere with the crystallisation and identification of the osazones are removed on the charcoal. With this method glucosazone is obtained in aqueous solutions of glucose, and in solutions of glucose in urine from which the normal sugars have been removed, in concentrations as low as 1 mgrm. per 100 c.c. In suitable cases glucose added to ordinary urines can be detected when the amount added is as low as 2.5 mgrms. per 100 c.c. Normal urines give numerous types of crystal mixtures, formed of a mixture of 2 simple osazones; one of these is identical with glucosazone, and the other appears to correspond with the *iso*-maltosazone of Baisch (*Z. physiol. Chem.*, 1895, 20, 249), as regards melting point, but differs markedly in crystalline appearance. The urines of over 700 Egyptians have been examined under different conditions, and it has been found that typical glucosazone crystals are given by 20 to 30 per cent. of the urines voided 1 to 2 hours after an ordinary meal; the percentage drops to 12 to 15 in urines passed 4 to 5 hours after meals, and to about 7 per cent. after a 12 hours' fast. An examination of the tolerance of 28 students to 50 grms. glucose has shown that, in most cases, this is not due to an abnormal carbohydrate metabolism. The excretion of glucose after 50 grms. have been taken seems to be less than that which follows an ordinary mixed meal. It is shown that some of the "physiological osazones" of Höst (*J. Metab. Res.*, 1923, 4, 315) are impure crystal mixtures, and possibly the same applies to some of the osazones of Geelmuyden (*Norsk. Mag. Laegevidenskaben*, 1915, 13, 985). The results presented leave little doubt that the old view that glucose in small quantities is a constituent of normal urine is confirmed. Photographs of some of the crystalline forms obtained of the osazones are reproduced. P. H. P.

Colorimetric Method for Determination of Lipoidal Phosphorus in Blood. S. L. Leiboff. (*J. Biol. Chem.*, 1928, 80, 211-214.)—A method is described for the determination of lipoidal phosphorus in small amounts of blood. The lipoidal material is extracted from oxalated blood with the alcohol-ether mixture of Bloor (*J. Biol. Chem.*, 1918, 36, 33), which was found to give the best results out of the various solvents tried. The alcohol-ether is then evaporated on the water bath, and the organic matter is destroyed with concentrated sulphuric acid and hydrogen peroxide. The excess acid is neutralised with ammonia and the liquid reacidified with acetic acid. The phosphate is then precipitated with uranium acetate and

determined colorimetrically by a procedure recently described by Leiboff (*J. Biol. Chem.*, 1928, **79**, 611; *ANALYST*, 1928, **53**, 863). Sulphuric acid followed by hydrogen peroxide was found to be more satisfactory for the digestion of lipoidal material than the sulphuric-nitric acid mixture used by some other workers. Although 0.1 c.c. of concentrated sulphuric acid destroys completely all the lipoidal extract from 0.5 c.c. of blood, yet 0.3 c.c. is used because it shortens the heating time, and more completely covers the sides of the tube (where lipoidal matter has been left during evaporation of the alcohol-ether mixture) during rotation. No super-heating and no loss of phosphorus occur in this method. Some details of the method, and the preparation of reagents are omitted, as they have been described in the previous publication. It is well known that the phosphorus content of an alcohol-ether extract is not a true measure of the lipoidal content, since other substances containing phosphorus, not lipid, are extracted along with the lipoids, but this is the only means available, since isolation of lipoids in a pure state is a matter of great difficulty, and impossible in small amounts of tissue.

P. H. P.

Note on Volatile Sulphide from Muscle. W. A. Osborne. (*Biochem. J.*, 1928, **22**, 1312.)—When the leg muscles of a well-nourished, recently killed guinea-pig were cut into small pieces and boiled immediately in water in a distillation flask, the delivery tube of which dipped into lead acetate solution, no volatile sulphide could be detected; if, however, about 24 hours had elapsed between the killing of the animal and the removal of the muscles, the presence of sulphide in the distillate was obvious, even when various procedures were adopted to remove the possibility of bacterial decomposition. Apparently, therefore, autolysis makes a change in the muscle proteins whereby loosely bound sulphur is produced or liberated. Sulphide was readily detectable in muscle from a recently killed guinea-pig which had been starved for 48 hours; the flesh of sheep in poor condition also emitted sulphide readily on boiling, but the same was not found with beef. Probably the muscle of different animals varies considerably in this reaction. P. H. P.

Determination of Carnosine. W. M. Clifford and V. H. Mottram. (*Biochem. J.*, 1928, **22**, 1246–1252.)—The method of Clifford (*Biochem. J.*, 1921, **15**, 400; *ANALYST*, 1921, **46**, 507) for the determination of carnosine, based on the colour produced when carnosine reacts with diazobenzene-sulphonic acid, and the application of the method to the chromogenic substances in muscle (*Biochem. J.*, 1921, **15**, 725; 1922, **16**, 341; 1922, **16**, 792; 1923, **17**, 549; *ANALYST*, 1922, **47**, 266; 1922, **47**, 443; 1923, **48**, 184) have been severely criticised by Hunter (*Biochem. J.*, 1921, **15**, 689; 1922, **16**, 640; 1924, **18**, 408; *ANALYST*, 1922, **47**, 266; 1923, **48**, 34) and by Mitsuda (*Biochem. J.*, 1923, **17**, 630). The method has therefore been reinvestigated, and the experimental work has been shared, so that one author has handed over clear, colourless solutions to the other for determination, the source, previous history and carnosine content of which were quite unknown to the receiver. Results show that the original carnosine upon which the work was based was chemically pure, and not, as has been suggested,

only 43 per cent. pure, the stock solutions of dyes once standardised were satisfactory, as they keep over a number of years, and that the method of determination has a high order of accuracy ; by this method the carnosine content of a solution of pure carnosine in water can be determined with an error of less than 1 per cent. With the use of this method to determine the chromogenic substances in samples of muscle, it has been shown that they vary in amount directly as the amount of muscle taken, no matter what skeletal muscle is used, nor if it is from a different animal of the same species, *i.e.* for the skeletal muscle of a species the carnosine content is a constant. This constant varies from species to species, but not from member to member of that species. A series of determinations of the chromogenic substances has been made on 13 different muscles or groups of muscle in the ox, and 9 different muscles and 4 groups of muscle in the cat. This work confirms the previous observations of Clifford on the muscles of rats, rabbits, calves, sheep and lambs. Hunter and Mitsuda, however, claim to have found differences in carnosine content between muscle and muscle and cat and cat. P. H. P.

Determination of Silica in Tissues. E. J. King. (*J. Biol. Chem.*, 1928, 80, 25-31.)—A micro method is described for the determination of silica in animal tissues, which depends on the intense yellow colour of silicomolybdic acid, produced when a silicate solution is treated with ammonium molybdate and sulphuric acid. The method is quick and easily applied, and the proportionality of colour produced in test solutions prepared from sodium silicate and from ashed tissue holds over a wide range of concentration. The yellow colour is of the same tint as that of a dilute solution of picric acid, and thus an artificial standard is possible ; it is also preferable, since a sodium silicate standard tends to deposit silica, and is difficult to standardise. The picric acid standard remains unchanged for at least 2 months, and can be made from any good brand of C.P. picric acid without recrystallisation. Where the phosphorus content is low, the silica present may be determined fairly reliably without precipitation of the phosphate, but for an accurate determination the removal of phosphate is necessary, and is accomplished by the addition of magnesia mixture to the solution of the ash, and the filtering off of the magnesium ammonium phosphate. It is shown that the silica is not partly precipitated with the phosphate, but is quantitatively determined by this method. An amount of tissue 0.2 to 1.0 grm. is a convenient quantity for a determination, and Hahn tubes, or graduated cylinders with stop-cocks near the bottom, mounted over white cardboard, form an inexpensive colorimeter. A table shows the silica content of some tissues which have been determined. P. H. P.

Irradiation of Ergosterol. T. A. Webster and R. B. Bourdillon. (*Biochem. J.*, 1928, 22, 1223-1230.)—The work recorded by Rosenheim and Webster (*Lancet*, 1927, 213, 622 ; *ANALYST*, 1927, 52, 652) has been continued in search of a possible means of isolation of vitamin D. The effect was studied of the use of " filtered " light (obtained by means of an alcoholic cobalt chloride filter) at various temperatures, in an attempt to produce more concentrated preparations of vitamin D. It seems reasonable to conclude from biological tests of the antirachitic activity

that the exclusion of wave-lengths shorter than $265\mu\mu$ (which were cut out by the filter) does not seriously alter the ratio of rates of production and destruction of vitamin *D*. This suggests, but does not prove, that vitamin *D* either has strong absorption for wave-lengths longer than $265\mu\mu$, or has not great absorption for wave-lengths of 230 to $250\mu\mu$, as suggested by previous workers. From the lack of marked effect of changes of temperature between $+78^{\circ}\text{C}$. and -18°C . on the equilibrium, the temperature coefficients of the changes which cause destruction and production are not widely different, and the moderate effect of lowering the temperature to -180°C . suggests that the temperature coefficient of both reactions is very small; hence both reactions are directly photochemical in nature. After the removal of unchanged ergosterol (as ergosterol digitonide) from solutions irradiated for short periods only, the products obtained formed a transparent, glassy hard solid of indefinite m.pt. beginning about 30°C ., at times colourless, but often contaminated with a yellow pigment. In contrast to the small (0.2 per cent.) solubility of ergosterol in alcohol, the product is soluble in its own weight of alcohol at 30°C . It shows high antirachitic activity, which varies considerably in different samples, as does the absorption spectrum; the presence of traces of yellow pigment showed strong absorption between 300 and $400\mu\mu$. From numerous attempts to find a quantitative relation between the magnitude of the absorption coefficients of the products described and their antirachitic activity, the following conclusions are reached:—If a 0.1 per cent. solution of ergosterol in alcohol or ether is irradiated at room temperature as described, products which have an antirachitic activity and absorption of the type described by the authors are present to a small extent after 30 seconds' irradiation, to a marked extent after 1 minute's irradiation, and to about 10 times this value after 10 minutes' irradiation, whilst for irradiation periods of between 10 and 60 minutes both properties increase to about 2 or 4 times their value after 10 minutes' irradiation. Therefore both antirachitic activity and absorption are produced at approximately the same rate and both begin in the earliest stages. Both decrease if the products of irradiation after removal of ergosterol are exposed to ultra-violet light, and disappear almost entirely after between 3 and 5 hours' irradiation under the above conditions. No product showing either antirachitic activity without the type of absorption described, or *vice versa*, has yet been obtained. A type of absorption which may be a property of vitamin *D* is shown in a curve. As the most probable explanation of the observed phenomena, it is suggested that the irradiation of ergosterol produces two substances in succession, of which the first has an absorption maximum at about 280 or $290\mu\mu$, and the second a maximum at about $230\mu\mu$, and that the former is vitamin *D*. Plates of the photographed absorption spectra are reproduced.

P. H. P.

Antirachitic Substances. VIII. Studies on Highly Purified Ergosterol and its Esters. C. E. Bills and E. M. Honeywell. (*J. Biol. Chem.*, 1928, 80, 15–23.)—A procedure was designed to prepare ergosterol of the greatest possible purity for research on antirachitic activation. Crude yeast sterol was obtained

from the unsaponifiable fraction of the fat of the common yeast, *Saccharomyces cerevisiae*, and it has been shown on examination to be a mixture of at least three sterols, separable with difficulty. Ergosterol itself is the main component, another is dextrorotatory and of low m.pt., and possibly identical with the zymosterol of MacLean (*Biochem. J.*, 1928, **22**, 22), and the third, named cerevisterol, is laevorotatory, and melts above 240° C. The ergosterol of yeast is identical with that of ergot obtained by Tanret (*Ann. chim. et phys.*, 1908, **15**, 313), and has been isolated in pure form. Previous workers have failed to get satisfactory purification, but purification has now been accomplished in two ways—by recrystallisation from an exceptionally effective solvent mixture (alcohol-benzene, 3:1), and by saponification of purified ergosteryl isobutyrate. Pure ergosterol exhibits in chloroform $[\alpha]_D^{20} = -132^\circ$ and $[\alpha]_{5461}^{20} = -171^\circ$. The high specific rotation is not due to admixture with the two contaminant sterols, for the specific rotation of the contaminants is low. The melting point is of little significance as an index of purity, for it varies from 166–183° C., according to the hydration of the sample. It would seem that the recent discoveries in the relation of ergosterol to vitamin D have all been made with ergosterol of questionable purity, since until now only Tanret had prepared ergosterol free from contamination. However, it has been found that the spectrographic and physiological properties associated with ergosterol of ordinary purity are exhibited by ergosterol free from contaminants. Pure ergosterol, unlike zymosterol and cerevisterol, is highly activatable, and shows the absorption bands found for ordinary ergosterol. More properties of pure ergosterol not given by Tanret in his report are described. Three new esters, ergosteryl isobutyrate, isovalerate, and cinnamate have been prepared and purified.

P. H. P.

Conditions of Formation and Destruction of Vitamin D on the Irradiation of Ergosterol. D. Van Stolk, E. Dureuil and Heudebert. (*Comptes. rend.*, 1928, **187**, 854–856.)—Elimination of waves of shorter length than 2550 Å during the irradiation of ergosterol did not stop the decomposition of the vitamin D formed, but irradiation of the alcoholic solution in an atmosphere of nitrogen considerably retarded the process, so that the final destruction of the vitamin is looked upon as due to oxidation and not to any destructive radiations. The absorption bands noted for the pure ergosterol had their maxima at 2932, 2815, 2700, and 2600 Å. The first three disappeared during irradiation, whilst the fourth became augmented, and two new bands at 2503 and 2405 Å also appeared, these latter being characteristic of vitamin D.

D. G. H.

Vitamin A Content of the Unsaponifiable Matter of Liver Oils. I. S. Meno, M. Yamashita and Y. Ota. (*J. Soc. Chem. Ind., Japan*), 1928, **31**, 281B.)—The authors report a large amount of vitamin A in the liver oil of "ishinagi" fish, *Stereolepis ischinagi* (Hilgendorf). After saponification the unsaponifiable portion from 100 grms. of the oil was extracted from the aqueous medium with ether, washed with water, and final traces of potash removed by precipitation with carbon dioxide. For applying the vitamin tests the purified dry product was dissolved in 100 grms. of olive oil. Growth curves are given for

albino rats fed on a basal diet of 69 parts rice starch, 5 parts cane sugar, 10 parts fat-free horse-flesh, 5 parts McCollum and Simmonds' salt mixture 185, 1 part "oryzanin" powder (vitamin *B*), and 10 parts of sample oil. It is shown that the vitamin *A* content of "ishinagi" liver oil is several hundred times that of cod-liver oil. The most rapid and reliable colour test for vitamin *A* is to add dried Japanese acid clay to 1 grm. of the oil dissolved in 10 c.c. of benzene. A violet coloration indicates the presence of vitamin *A* (see Abstract, p. 65).

R. F. I.

Synthesis of Vitamin *B* in the Rumen of the Cow. S. I. Bechdel, H. E. Honeywell, R. A. Dutcher and M. H. Knutsen. (*J. Biol. Chem.*, 1928, 80, 231-238.)—It has been shown by Bechdel, Eckles and Palmer (*J. Dairy Sc.*, 1926, 9, 409) that a calf will grow normally to maturity and produce normal offspring on a ration that carries an insufficient amount of the vitamin *B* complex to support growth and well-being in rats; also, by Bechdel and Honeywell (*J. Agric. Research*, 1927, 35, 283) that vitamin *B* in milk is not dependent on the presence of this vitamin in the ration of the cow. It thus appeared that cattle, and possibly all other ruminants, can synthesise vitamin *B*, and so experiments were designed to determine whether the micro-organisms present in the rumen of an experimental cow were responsible for the synthesis of vitamin *B* complex. Investigations were conducted on the fermented rumen contents of a Holstein cow, representative of a group of 17 animals that were grown to maturity on a ration highly deficient in vitamin *B* complex. A permanent fistula about 3½ inches in diameter was made in the rumen of the experimental heifer through the left side; it was kept tightly closed in order that normal conditions could be maintained within, and with this means the rumen contents could be sampled easily. Alcoholic extracts of the fermented rumen contents were proved potent in the vitamin *B* complex through rat-feeding trials; therefore vitamin *B* must have been synthesised by bacteria or other micro-organisms. One bacterium of the genus *Flavobacterium* was found to predominate to the extent of about 90 per cent. in the rumen microflora which were next examined. As no account of it was found in the literature, it is described, and is called *Flavobacterium vitarumen*. This organism was grown in large quantities on vitamin *B*-free media and given to rats to the extent of about 12 per cent. of dried bacterial cells in a synthetic vitamin *B*-free ration. The bacterial cells were proved to be highly potent in the vitamin *B* complex. It is therefore concluded that the vitamin *B* complex was produced in the rumen of the experimental cow by bacterial fermentation; this offers a satisfactory explanation as to why cattle, unlike any other species of animal yet studied, can grow to maturity, produce normal offspring, and produce milk of normal dietary composition, on a ration that has not sufficient vitamin *B* complex to support growth and well-being in rats.

P. H. P.

Toxicological and Forensic.

Toxicological Study of Bismuth. R. Fabre and M. Picon. (*J. Pharm. Chim.*, 1928, 120, 297-308.)—Oil solutions of bismuth camphocarbonate were injected by the intra-muscular or intravenous method into rabbits and dogs, and it was found that the bismuth was retained in important quantities by the liver

and kidneys, but only in minimum quantities by the brain. The kidneys retained more bismuth than the liver, and death was probably, at least partly, due to alteration in the renal functions. Elimination was by means of the kidneys, but salivary excretion and excretion by the skin also play a very important part.

D. G. H.

Arsenic Test of the German Pharmacopoeia. G. Frerichs. (*Pharm. J.*, 1928, 121, 383.)—The solution of sodium hypophosphite in fuming hydrochloric acid, which in the German Pharmacopoeia VI has replaced Bettendorf's reagent for testing for arsenic, is incorrectly named, as it contains, not hypophosphite, but free hypophosphorous acid with a small quantity of sodium chloride. The author proposes to name this reagent "Thiele's hypophosphite solution," and regards it as superior to stannous chloride solution, except perhaps for the examination of iron preparations, where the colour interferes, owing to incomplete reduction of the ferric oxide. This difficulty may be overcome by addition of a sufficiently large quantity of stannous chloride solution, and the test then admits of the detection of 0.00001 grm. of arsenic in 1 c.c. of ferric chloride solution. Potassium iodide may also be used for decolorising ferric solutions. In testing *sulphur sublimatum* and *praecipitatum* the troublesome treatment with nitric acid may be avoided by following the slightly modified test of the German Pharmacopoeia V: 2 grms. of the sulphur are shaken vigorously in a flask with 10 c.c. of ammonia solution and heated on a water-bath at 40° to 50° C. for about five minutes, 5 c.c. of the filtered liquid being then evaporated to dryness. The residue is dissolved in three or four drops of sodium hydroxide solution and 5 c.c. of hydrogen peroxide solution, the liquid being again evaporated to dryness and the residue dissolved in about 1 c.c. of dilute hydrochloric acid and heated with 3 c.c. of the hypophosphite solution in a boiling water-bath for fifteen minutes; the liquid should remain clear and colourless.

T. H. P.

Detection of Arsenic. Dauvé. (*Ann. Chim. analyt.*, 1928, 10, 320–321.)—It is recommended that in using Gatehouse's method for detecting arsenic, as described in Wurtz's Dictionary (Supplement, p. 240), mercuric chloride should replace the silver nitrate in making the test paper, since silicon hydride is formed under the conditions of experiment from the silica present in the aluminium, and whilst this blackens silver paper it has no effect on the mercury solution. The solution to be tested is placed in a bottle in the neck of which is suspended a glass tube, lightly closed at the end with cotton wool, and with a hole at the side for the entrance of the hydrogen arsenide, and in which is suspended the test paper, moistened with only one drop of mercuric chloride, to give a contrast of colour.

D. G. H.

Bacteriological.

Determination of the Number of Organisms in Water. W. Plücker and W. Bartels. (*Z. Unters. Lebensm.*, 1928, 56, 51–60.)—The current (German) methods for the determination of the number of organisms in water are discussed

in the light of the recommendations of numerous workers. Prall's medium, which is a meat extract and peptone-salt mixture, containing 5 per cent. of gelatin and 0.75 per cent. of agar, is recommended in addition to those ordinarily used. A P_R value of 7.0 to 7.1 is suitable for the harmless water bacteria, as well as for *B. coli*, *B. alcaligenes*, *Staphylococcus pyogenes* and *Paratyphus*, though *B. typhi* requires P_R 7.2 to 7.9. An incubation period of 48 hours at 20 to 22° C. is recommended, and Brudny's automatic apparatus (*Zentr. f. Bakt.*, 1911, 57, 478) has been found useful for counting the colonies. The microscopic method of Hesse-Niedner (*Z. Hyg.*, 1904, 20, 119) is more sensitive, the number of colonies per c.c. of water being given by the formula D^2vm/d^2 , where D is the diameter of the Petri dish (90 to 94 mm.), v the dilution of the water, and m the number of colonies in the field of vision of the microscope (diameter d mm.). The thickness of the layer of medium should not exceed 1.5 mm., corresponding with 9 c.c. of liquid. J. G.

Gas Production in the Making of Sauerkraut. L. M. Preuss, W. H. Peterson and E. B. Fred. (*Ind. Eng. Chem.*, 1928, 20, 1187, 1190.)—The gas evolved during the formation of sauerkraut consists of almost pure carbon dioxide, and most of the gas is given off within forty to one hundred and sixty hours after the cabbage has been packed in the container. The fermentation is more rapid at higher temperatures (25° to 28° C.) than at lower temperatures, and there is a close relation between the volume of gas, numbers of bacteria, and acidity, denoting that the gas production is due to bacterial action and not to yeast growth.

W. P. S.

Organic Analysis.

New Oxidation Reactions of Aldehydes. J. B. Conant and J. G. Aston. (*J. Amer. Chem. Soc.*, 1928, 50, 2783–2798.)—Oxidation of isobutaldehyde by alkaline potassium ferricyanide solution at 80° C. gives 2:2:5:5-tetramethyldihydropyrazine and 2:2:5:5-tetramethyl-3:6-dicyanopiperazine, but no isobutyric acid; under similar conditions, methyl isopropyl ketone is oxidised to hexamethyldihydropyrazine. When oxidised in acid solution by either ceric sulphate at 80° C., or potassium permanganate at 80–90° C., or cobaltic sulphate at 0° C., isobutyraldehyde yields acetone, α -hydroxyisobutaldehyde, and isobutyric acid, whilst chloranil in presence of palladium black slowly oxidises the aldehyde to α -hydroxyisobutaldehyde. In acid solution at 80° C., potassium dichromate oxidises isobutaldehyde in the α -position, giving acetone to the extent of 40 per cent. in solutions of high dilution, which favours the oxidation; *n*-butaldehyde also is oxidised in the α -position, carbon dioxide being formed. Potassium permanganate oxidises acetaldehyde in acid solution at 80° C., giving carbon dioxide as well as acetic acid if the reactants are kept very dilute and the aldehyde is in excess.

T. H. P.

New Procedure for the Separation of Alcohols and Phenols from Oil Mixtures. H. Schmidt. (*Chem. Ztg.*, 1928, 52, 898.)—The oil mixture is warmed at 80 to 100° C. in a distillation-flask with the approximate amount of boric acid

required to form the triboric ester $B(OR)_3$, and the water produced is distilled over in a low vacuum. The vacuum is then raised till the oil has distilled off, the residue saponified with sodium hydroxide solution, and the liberated phenol or alcohol removed by steam distillation. Solid borates, which often denote the presence of cyclic alcohols, may be recrystallised. Boric anhydride, triaceto-boric acid $B(O.COCH_3)_3$, arsenic, antimonie or phosphoric acids may also be used, and the method is preferable to the benzylation or acid ester methods, in that it is simple, inexpensive, rapid and quantitative. Since primary, secondary and tertiary alcohols are esterified with progressive difficulty, they may be separated by fractional esterification with determined amounts of boric acid. Borneol and dihydroterpineol were isolated from American pine oil (*Ber.*, 1928, 60, 1372), whilst menthol and menthone (*id.*, 1926, 59, 2306), and geraniol and citral were among other substances separated from one another. J. G.

Use of Iron Reagents in the Detection and Differentiation of Phenols.

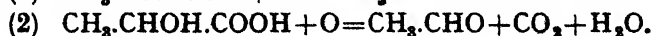
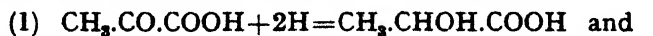
A. H. Ware. (*Quart. J. Pharm.*, 1928, 1, 377-387.)—The phenols are divided into 3 classes: Class A, consisting generally of phenols giving only one definite colour reaction with ferric salts; Class B, possessing two or more hydroxyl groups in contiguity and giving colour changes with ferric chloride largely determined by P_H concentration, but in a series of five colours; and Class C, containing pyrone and quinonoid phenols, and giving with ferrous salts and weak alkali an intense brown colour. In practical work Mitchell's reagent (0.1 grm. ferrous sulphate and 0.5 grm. of Rochelle salt in 100 c.c. of water) is used with decreasing P_H , and ferric chloride with increasing P_H . Mitchell's reagent (*ANALYST*, 1923, 48, 2) is more satisfactory than ordinary ferrous salts, because the P_H is very near 7; ferrous or ferric hydroxides, basic ferric acetate or phenol-iron-complexes may be eliminated, but the controlled precipitation in bulky filterable form of certain complexes may be brought about when necessary; very little ferric iron is present, and maximum intensities of colour for Classes B and C may be obtained by appropriate adjustment of the P_H . The reagent is added until no further darkening occurs, the P_H adjusted with very dilute ammonia or sodium bicarbonate solution, and, if a negative result is obtained, the phenol is placed provisionally in Class A; a violet colour indicates Class B, and a deep brown Class C. Potassium acetate is then added and the mixture boiled, when tannin is precipitated. Haemotoxylin is partly precipitated (blue), and also maclurin and many anthroxanthins, as brown complexes. For the ferric chloride test, a 1 per cent. so-called neutral solution is added, drop by drop, to the solution of the phenol; the results with a large number of phenols are described. Special tests are as follows:—One or two drops of liquid phenol or a pinch of solid is dissolved in 5-10 c.c. of water together with a little ferrous sulphate; 1 drop of 10 volume hydrogen peroxide is then added, and the mixture shaken until a marked degree of green, red or brown colour is given, whichever appears first. The mixture is then shaken with from 0.2-0.5 grm. of sodium sulphite.

Name of Phenol.	Result before adding sodium sulphite.	Result after adding sodium sulphite.
Carbolic acid, the cresols (including B.P. cresol)	Deep green	Blue, violet or purple
Guaiacol and B.P. creosote	Brownish green	Brown " "
Salicylic acid and other salicyl bodies	Purple	Brown " "
Thymol and eugenol (in alcoholic solution)	Not distinctive	Not distinctive
Hydroquinol	Reddish colour	Blue, violet or purple
Resorcinol and orcinol	Brown	" " " "
Phloroglucinol	Yellow, greenish or brown	Brown or "yellow"
Aloin and phloridzin	Brown, or reddish	Brown

Test for isocarbon.—To a pinch of aloes dissolved in 5–10 c.c. of water and filtered, is added one drop of hydrogen peroxide, and, after shaking, 1 per cent. ferric chloride solution, drop by drop, with shaking after each drop, when the colour changes are: green \rightarrow brown \rightarrow ruby red \rightarrow reddish purple. A precipitation test for certain phenols is carried out in 5 steps with Mitchell's reagent, or a solution of citrate of iron and ammonia, with subsidiary reagents Rochelle salt, ammonium hydroxide, 35 per cent. acetic acid, and a 35–40 per cent. solution of formaldehyde. Details and results are tabulated. Clearly-defined stages are present at which typical pure gallo-tannins, phlobatannins and phenols of Class B are precipitated and pyrogallol tannins are distinguished from all other plant principles.

D. G. H.

Determination of Pyruvic Acid. B. H. R. Krishna and M. Sreenivasaya. (*Biochem. J.*, 1928, 22, 1169–1177.)—The methods used for the determination of pyruvic acid are largely based upon the reaction of its carbonyl group with phenylhydrazine; its determination in complex biological fluids where there are other compounds which react similarly is therefore difficult, particularly when the pyruvic acid is present only in small quantities. The authors have made a study of some of the existing methods, but found none suitable without modifications for their work, *i.e.* for determinations of small quantities of the acid in solutions of very low concentration. They have developed a new method, more specific when applied to biological fluids, which is a modification of the technique of Lieben (*Biochem. Z.*, 1923, 135, 240), and is based upon the reactions:



It is shown that the reduction of pyruvic to lactic acid with the use of a zinc-copper couple in sulphuric acid solution, oxidation of lactic acid by a slight modification of the recent method of Friedmann, Cotonio and Schaffer (*J. Biol. Chem.*, 1927, 73, 335; *ANALYST*, 1927, 52, 418–419), with the use of a simpler apparatus, and titration of the bound aldehyde according to the method of Clausen (*J. Biol. Chem.*, 1922, 52, 263; *ANALYST*, 1922, 47, 363) gave quite constant results over a large range of pyruvic acid concentrations. Although the aldehyde yield was small,

the error was quite regular, as shown by tables of results. By means of an empirical factor, *i.e.* 1 c.c. $N/10$ iodine represents 5.5 mgrms. of pyruvic acid—the exact amount of pyruvic acid can be computed. The following technique is advised when the method is applied to biological fluids:—The solution should not contain more than 15 mgrms. of pyruvic acid during its reduction to lactic acid; about 2 to 5 c.c. of an approximately 0.05 per cent. solution is used for protein separation either by ether extraction or alcoholic precipitation, and the whole of the filtrate is taken up for subsequent processes. The filtrate is rendered neutral to litmus and evaporated under diminished pressure at 40 to 50° C. The substance is then transferred to an extractor with a small quantity of saturated ammonium sulphate solution, rendered slightly acid, and extracted with ether. The ether extract is evaporated to dryness, shaken up with excess sodium bisulphite, and again extracted. The residue is transferred to a 100 c.c. flask, the pyruvic acid reduced to lactic acid by sulphuric acid and zinc with a trace of copper, and the lactic acid is then determined. The probable error of a single determination has been found to be about 1.4 per cent.

P. H. P.

Lehmann's Method for the Determination of Aniline. A. V. Pamfilov and V. E. Kisseleva. (*Z. anal. Chem.*, 1928, **75**, 87–92.)—The method described in "Chemisch-technische Untersuchungsmethoden," 1921, p. 657 (G. Lunge and E. Berl) has been examined and modified. The aniline is absorbed in 10 per cent. sulphuric acid, and 20 c.c. of 0.8 to 0.0006 N sodium hypobromite solution (prepared by the addition of sodium hydroxide solution to 0.4 per cent. bromine water till the yellow colour disappears), and 1 to 2 grms. of potassium bromide are added. After 3 minutes in a stoppered bottle the solution is back-titrated with 0.1 to 0.001 N sodium thiosulphate solution in the presence of potassium iodide, with starch as indicator. Satisfactory results were obtained for 0.05 M aniline sulphate solutions. For more dilute solutions (0.005 to 0.00005 M) the weaker reagents are used with indigo carmine as indicator, but the results are progressively high as the concentration decreases.

J. G.

Reactions of Dyestuffs with Nitrous Acid. J. V. Dubský and A. Okáč. (*Z. anal. Chem.*, 1928, **75**, 92–111.)—The use of the coloration produced by diazotisation, with or without subsequent coupling with suitable reagents, for the colorimetric detection of nitrous acid, has been tested for about 100 dyestuffs of varied constitution. A sensitiveness of $1:10^6$ to $1:10^7$ was usually found, and a table shows the colours of the solutions before and after treatment with nitrous acid, and also after coupling with one or more of 23 suitable compounds, together with the sensitiveness of the reaction concerned. As a rule, α -compounds with a free para-position gave a faster reaction and a deeper colour, and were about 10 times more sensitive than β -compounds with a free ortho-position (*cf.* Vaubel, *ANALYST*, 1928, **53**, 674).

J. G.

Chemistry of Jaffe's Reaction for Creatinine. V. Isolation of the Red Compound. I. Greenwald. (*J. Biol. Chem.*, 1928, **80**, 103–106.)—The new dicreatinine compound described by Greenwald (*J. Biol. Chem.*, 1928, **77**, 539;

ANALYST, 1928, 53, 400-401) was proved not to be the substance responsible for Jaffe's reaction. It had previously been shown by Greenwald and Gross (*J. Biol. Chem.*, 1924, 59, 601; ANALYST, 1924, 49, 346) that although only 1 molecule of picric acid entered into the reaction, the maximum colour in Jaffe's reaction was not obtained unless at least 2 molecules of picric acid were present. It was therefore thought of interest to ascertain what might be precipitated when an alkaline mixture containing 2 molecules of picric acid for each molecule of creatinine was run into alcohol. The first preparation yielded a red precipitate which seemed to be a mixture of the dicreatinine compound and a new one containing 1 molecule of creatinine, 1 of picric acid and 2 of sodium hydroxide. With the use of a little more picric acid (2.5 or 3 molecules), and not too great an excess of sodium hydroxide, the new compound was obtained nearly pure. After drying *in vacuo*, the substance forms a brilliant red, hygroscopic powder. When dissolved and diluted in water to contain 10 mgrms. of creatinine per 500 c.c., and compared with 0.5 *N* potassium dichromate, the colour obtained corresponds to only about 20 per cent. creatinine instead of the calculated 26.8 per cent.; this is probably due to dissociation, for, if a mixture of 15 c.c. of 1 per cent. picric acid and 5 c.c. of 10 per cent. sodium hydroxide is added before dilution, the full colour is obtained immediately. Therefore it is the formation of this compound that is responsible for the red colour of Jaffe's reaction. This does not altogether contradict the previous view that the formation of the red tautomer of creatinine picrate gives the colour, for the new compound may be regarded as a compound of the red tautomer with 2 molecules of sodium hydroxide. Hydrochloric acid precipitates the red tautomer from fairly concentrated solutions of the new compound. A solution of the new compound gives a red precipitate with basic lead acetate solution. When filtered, washed, and dried over sulphuric acid, the composition of the precipitate agrees closely with that calculated for a compound of 1 molecule of creatinine, 1 of picric acid, 2 of lead hydroxide, and 2 of water. As with the dicreatinine compounds, both the sodium and the lead compound contain more base than the formulae would require. With the high equivalent weight of lead, this results in a decided effect on the creatinine and picric acid content. Differences in the behaviour of both the creatinine and the picric acid show that the nature of the combination between picric acid and creatinine in the new compounds is quite different from that in the dicreatinine compounds.

P. H. P.

Determination of Sulphur in Rubber by the Perchloric Acid Method.
E. Wolessensky. (*Ind. Eng. Chem.*, 1928, 20, 1234-1238.)—The following procedure is recommended: One grm. of the finely-divided sample is heated for two minutes in a 500 c.c. flask with 10 c.c. of 41 per cent. nitric acid; 10 c.c. of concentrated nitric acid are then added, and the heating is continued for fifteen minutes, or until the rubber has dissolved. Five c.c. of 60 per cent. perchloric acid are added, and the mixture is boiled until white fumes appear. It may be necessary to add more perchloric acid if free carbon is present, or, in the absence of other precipitates, the carbon may be removed by filtration. The clear solution

is then treated with 5 c.c. of concentrated hydrochloric acid, again heated, cooled, diluted, and the sulphate precipitated with barium chloride. If barium sulphate is present in the rubber, it is separated from the oxidised solution previous to the precipitation with barium chloride.

W. P. S.

Determination of Iron Carbonyl. R. H. Griffith and G. C. Holliday. (*J. Soc. Chem. Ind.*, 1928, 47, 311-312.)—The formation of iron carbonyl in water gas or coal gas stored under pressure in steel cylinders suggested the possible occurrence of the carbonyl in the mixture of carbon monoxide and hydrogen used for the synthesis of methyl alcohol. Such occurrence is actually observed, and catalyst which has been used in this synthesis is found to be stained with a brown deposit of iron. To determine iron carbonyl in a gas, this is passed through cotton wool and washed with sulphuric acid, which absorbs the carbonyl quantitatively. The acid is then evaporated to dryness, and the residue dissolved in hydrochloric acid and tested with ferrocyanide, the colour density of the uncoagulated Prussian blue formed being measured under standard conditions. For this purpose use is made of a modified Sanger-Shepherd density meter with a red light filter to convert the colour to neutral grey. A cell, 10 mm. wide inside, may be used to contain the solution, and a 100-watt Fullolite lamp as the source of light. The density wedge is first calibrated by means of a solution containing 0.1 grm. of iron, dissolved in slight excess of hydrochloric acid, per litre. Various volumes (between 0.5 and 10 c.c.) of this solution are placed in 50 c.c. graduated cylinders, 1 c.c. of concentrated hydrochloric acid (10 N) being added and the volume made up to 25 c.c. with water. One c.c. of 10-volume hydrogen peroxide is added to oxidise any ferrous iron, and the solution made up to 48 c.c.; 2 c.c. of 0.1 M potassium ferrocyanide solution are added, and the whole shaken. After the lapse of 10 mins., the cell is charged and the density reading taken. A table is given showing, for solutions containing quantities of iron varying from 0.00005 to 0.001 grm. per 50 c.c., the corresponding wedge readings and the densities of the "blue." The wedge reading may be determined to within 0.02, equivalent to 0.0002 mgrm. of iron. The conditions of the calibration must be adhered to strictly during the determination; the readings are affected considerably by increasing additions of acid or the presence of salts, and slightly by curtailing the time during which the liquid stands before the reading is taken. Concentrated sulphuric acid may be used in place of hydrochloric acid, provided that not more than 0.5 c.c. is taken.

The amounts of iron carbonyl, in grms. per 1000 litres, found in carbon monoxide from various sources, are: from the active-iron reaction tube, 1.26; from storage holders, compressed, 0.1853; stored at 80-100 atmos. for 6 months in a cylinder which had been in use for about 20 years, 0.00245; freshly made in Tantiron pots from sulphuric and anhydrous formic acids, 0.00844. Town gas contained 0.0003 grm. of the carbonyl per 1000 litres; in this case the absorption was effected by means of B.D.H. charcoal, since only a limited amount of this gas can be treated with sulphuric acid, owing to absorption of unsaturated compounds.

Methyl alcohol (either once distilled or "pure"), absolute alcohol (fermentation or synthetic), and nitric, sulphuric, and hydrochloric acids contain iron in small proportions.

T. H. P.

β -Methyl-umbelliferone as a Fluorescent Indicator. C. Bülow and W. Dick. (*Z. anal. Chem.*, 1928, 75, 81-86.)—About 2 drops of a 0.3 per cent. alcoholic solution of β -methyl umbelliferone (Pechmann and Duisberg, *Ber.*, 1883, 16, 2122) appear colourless in acid solutions, but give a strong blue fluorescence in alkaline solutions, which is visible against a background of black glazed paper without the aid of a quartz lamp. The end-point, which is masked in dark brown, but not in yellow, red or blue solutions, occurs at P_H 6 to 7, and the indicator is therefore best suited for the titration of strong bases against strong acids. For weak acids, however, back-titration may be used.

J. G.

Inorganic Analysis.

Rapid Method for the Determination of Selenium. E. Benesch. (*Chem. Ztg.*, 1928, 52, 878-879.)—The solution of selenium is reduced (e.g. by an acid solution of sodium bisulphite) and the amorphous selenium (0.2 to 0.3 gm.) filtered off, washed, and dissolved in 100 c.c. of a cold saturated solution of sodium sulphate. The red coloured solution and filter paper are placed in a flask, 150 c.c. of water added, and the whole titrated with a 0.1 *N* potassium cyanide solution (1 c.c. = 0.0079 gm. Se), which is standardised under the same conditions against a known weight of selenium. A change of colour to bright yellow, similar to that of methyl orange, indicates the end-point of the reaction $\text{Se} + \text{KCN} = \text{KCNSe}$.

J. G.

Determination of Palladium by 6-Nitroquinoline. S. C. Ogburn and A. H. Riesmeyer. (*J. Amer. Chem. Soc.*, 1928, 50, 3018-3022.)—The chloride solution is heated to boiling and treated with a hot saturated aqueous solution of the reagent. The mixture is stirred and boiled for a few minutes, and tested for complete precipitation by the addition of more reagent. The flocculent yellow precipitate is collected after 15 minutes, washed with water, dried, ignited carefully, reduced in hydrogen, and cooled in carbon dioxide. In presence of other platinum metals, the results show a negative error.

W. R. S.

Detection of Copper in Presence of Iron. L. Szebellédy. (*Z. anal. Chem.*, 1928, 75, 167-168.)—The addition of ammonium fluoride (1 gm.) to a solution of ferric iron (0.1 gm.) prevents the formation of the blue ferrocyanide precipitate, a white precipitate being formed. The precipitation of copper ferrocyanide is not impeded, hence a fraction of a mgrm. of copper imparts a pink tinge to the white iron precipitate.

W. R. S.

Modification of Low's Short Iodide Method for Copper. H. F. Bradley. (*Chemist Analyst*, 1928, 17, 14.)—Low's method (*Technical Methods of Ore Analysis*, p. 85) gives good results for ores of high manganese content if modified as follows:—To 0.5 gm. of ore are added a few drops of water, a little potassium chlorate,

5 c.c. of nitric acid, and a drop of hydrochloric acid, and the mixture heated for 5 minutes. Any brown oxides of manganese are dissolved in a few drops of a mixture of hydrogen peroxide and hydrochloric acid, 7 c.c. of concentrated sulphuric acid added, and when copious fumes are evolved the solution is cooled, diluted to about 40 c.c., and again boiled. The cooled solution is then almost neutralised with 13 c.c. of ammonia and a strong solution of ammonium acetate added till the red ferric acetate appears. After the addition of a further 5 c.c. of the acetate solution, the red colour is dispersed with sodium fluoride (0.5 gm.), and the solution titrated in the usual way in the presence of 3 grms. of potassium iodide. J. G.

Analytical Chemistry of Gallium. (Part I.) L. Moser and A. Brukl. (*Monatsh. Chem.*, 1928, 50, 657-668.)—Gallia is a much weaker base than alumina, from which it differs by yielding a ferrocyanide precipitate in strongly acid solution. Though not precipitated by hydrogen sulphide from acid solution, gallium is adsorbed by the sulphide precipitates of the heavy metals. Gallium is weighed as white sesquioxide, obtained by strong ignition of the hydroxide, nitrate, or sulphate in porcelain or silica, but not platinum (partial reduction through diffusion). The ignited oxide is hygroscopic, and should be weighed with dispatch. The ammonia precipitate is gelatinous like aluminium hydroxide, and soluble in caustic alkali; it is more soluble in ammonia than the aluminium precipitate, and the presence of ammonium salts increases the solubility. The precipitation of basic gallium acetate is quite incomplete; a large excess of ammonium acetate may prevent the precipitation altogether. The authors recommend tannin as the best and most sensitive precipitant for gallium (sensitiveness, 1:5,000,000). The boiling, weakly acid acetate solution containing 2 per cent. of ammonium nitrate, is stirred and treated, drop by drop, with a 10 per cent. solution of tannin till precipitation is complete: 10 parts of tannin suffice as a rule, but for minute amounts of gallium the tannin should be not less than 0.5 gm., otherwise the precipitate does not deposit readily. It is very bulky, hence with more than 0.1 gm. Ga_2O_3 it is of inconvenient size; if a large amount of gallium is to be precipitated, the bulk may be obtained as basic acetate, and the balance in the filtrate by tannin. The precipitate is washed with hot water containing a little ammonium nitrate and a few drops of acetic acid. Filter and precipitate are dried and ignited in porcelain to Ga_2O_3 , which is weighed. Ammonium chloride should not be used in the washing, as gallium chloride is volatile. The above procedure permits of the accurate separation of gallium from zinc (its most important mineral associate), nickel, cobalt, manganese, cadmium, beryllium, and thallium. The weakly acid (one per cent. acetic) solution is treated with ammonium acetate and two per cent. of ammonium nitrate, boiled, and precipitated with tannin as before. The precipitate is dissolved in hot dilute hydrochloric acid, and the precipitation repeated. Directions are given for recovering each of the other metals from the combined filtrates: zinc, cadmium, cobalt, nickel, and manganese, by hydrogen sulphide; beryllium, by tannin and ammonia (ANALYST, 1928, 402); and thallium, by

destruction of the tannin with fuming nitric acid, followed by precipitation of the chromate (*id.*, 1928, 459). (Separation of gallium from iron, *id.*, 1928, 558.)

W. R. S.

Oxalate Method for Separating Calcium and Magnesium. W. T. Hall. (*J. Amer. Chem. Soc.*, 1928, 50, 2704-2707.)—The results of the author's experiments confirm the view that excess of ammonium oxalate is required for the precipitation of calcium oxalate in presence of magnesium, and show that, if this excess is properly regulated, it is possible to precipitate pure calcium oxalate. If, however, a very large quantity of ammonium oxalate is present, the precipitation of magnesium ammonium phosphate is incomplete, even after long standing. For the precipitation of 0.3 grm. of calcium ions in a volume of 500 c.c., 75 c.c. of 0.5 N ammonium oxalate is sufficient, whereas the same quantity of this reagent is necessary for only 0.02 grm. of calcium in presence of a considerable amount (0.12 grm.) of magnesium.

T. H. P.

Detection of Potassium in Presence of Ammonium Salts. R. D. Reed and J. R. Withrow. (*J. Amer. Chem. Soc.*, 1928, 50, 2985-2987.)—A solution of zirconium sulphate (0.1131 grm. per c.c.; slightly acid) was found to detect 0.00048 grm. or more of potassium in 2 c.c. of solution in presence of a large amount of ammonium sulphate. In all other wet tests for potassium, ammonium is also precipitated. The procedure is the same as that used for the detection of potassium in presence of sodium (ANALYST, 1928, 456).

W. R. S.

Synthesis of Japanese Acid Clay. N. Kameyama and S. Oka. (*J. Soc. Chem. Ind. (Japan)*, 1928, 31, 269B.)—Analysis of Japanese acid clay shows it to contain 49.9 to 68.4 per cent. of silica, 9.8 to 20.9 per cent. alumina, and traces of iron, calcium, magnesium, and alkali metals. Preparations were made of pure silica gels dried under varying conditions, silica gels containing alumina in the proportion of 1 mol. Al_2O_3 per 6 mols. SiO_2 , and silica gels containing alumina and ferric oxide. In every case these preparations showed similar characteristics as Japanese acid clay, except one. They turned blue litmus red, liberated acid from potassium chloride solution, inverted cane sugar, absorbed methyl violet from solution, absorbed moisture from the atmosphere, and were coloured blue by contact with liver oil. Furthermore, heat was produced by wetting the powder with turpentine oil. But the preparations all lacked the power of oxidising an aqueous solution of benzidine base.

R. F. I.

Physical Methods, Apparatus, etc.

Determination of the Heat Value of Coal in Nickel-lined Bombs. A. E. Stoppel and E. P. Harding. (*Ind. Eng. Chem.*, 1928, 20, 1214-1218.)—To determine the amount of nickel dissolved from the bomb by the action of the nitric and sulphuric acids resulting from the combustion, the acidity of the bomb washings is titrated with 0.1 sodium hydroxide solution, methyl red being used as indicator.

The solution is then boiled and the titration continued, phenolphthalein being used as indicator. The number of c.c. of alkali solution used in the first titration is multiplied by 1.45 to give the correction, in calories, for the free acid; the quantity of alkali solution required in the second titration is multiplied by 4.50 to obtain the correction for the combined acid. To the sum of these two values are added 14 calories for each cgrm. of sulphur in the coal burned. W. P. S.

Carbon and Hydrogen Determinations with the Use of a Metal Tube. S. Avery. (*Ind. Eng. Chem.*, 1928, 20, 1232-1234.)—The tube described consists of a copper tube of about 15 mm. internal diameter, each end of which extends for about 3 inches from a thin, tightly fitting outer jacket of nickel tube. The two ends of the copper tube are provided with water-jackets through which a current of water is conducted, whereby the temperature is maintained between 60° and 80° C. The tube is durable, and the inner coating of copper oxide which forms is an advantage. Nickel tubes, or nickel-copper alloy tubes, would also appear to be suitable if they could be obtained free from carbon, but this does not seem to be possible. W. P. S.

Reviews.

LUNGE AND KEANE'S TECHNICAL METHODS OF CHEMICAL ANALYSIS. Edited by CHARLES A. KEANE and P. C. L. THORNE. Second Edition. Vol. II. Pp. xix+644. 1928. London: Gurney & Jackson. Price £3 3s.

In this volume of the revised edition of Lunge and Keane's well-known manual of analysis a considerable departure has been made in the arrangement of the subject matter, as compared with the first edition. Correlated industries have been grouped together in order to make the volume more self-contained, and the material has been divided into six sections dealing, respectively, with Iron and Steel (93 pp.), Non-Ferrous Metals (263 pp.), Metallic Salts (41 pp.), Potassium Salts (30 pp.), Paints and Pigments (134 pp.), and Paint Vehicles, Japans and Varnishes (60 pp.).

In the seventeen years which have elapsed since the first edition of this volume was published great advances have been made in analytical chemistry, and one would naturally expect to find evidence of these advances in such a classic as this book is now considered to be. In this respect the reader will be somewhat disappointed, for although much recent work is included, there are many obsolete methods described which might have been omitted to make room for fuller descriptions of more modern procedures. Especially is this noticeable in the section dealing with the non-ferrous metals which, in the reviewer's opinion, should have been entirely re-written and not merely revised by the addition of a few new methods and the omission of a paragraph or section here and there.

The section on Iron and Steel by Prof. C. O. Bannister contains methods for the analysis of iron and manganese ores, pig iron, malleable iron, steel, fluxes used in smelting and the various slags and by-products obtained in working up iron ores into the finished steel product. All the well-recognised standard methods are given, including procedures for the analysis of the numerous special steels, the introduction of which constitutes one of the greatest advances made in the metallurgy of steel during the present century. New features of this edition, therefore, supply details for the determination of cobalt titanium, zirconium, uranium, cerium, boron, and nitrogen in steel; Pickard's method of determining oxygen in steel is also given, but no reference is made to the work of Oberhoffer and his collaborators on the determination of the various oxide and slag inclusions.

Mr. G. Patchin has collaborated with Prof. Bannister in writing the section on the non-ferrous metals. This follows closely the corresponding section in the first edition, except that the chapters on tantalum and thorium have been omitted. Among the many obsolete methods which still find a place here are those of Deville and Debray and of the St. Petersburg Mint for the analysis of platinum ores, which are now of historic interest only, while those of Hess and Miller are far too unreliable now that extreme accuracy is required, owing to the high price of the metals. The methods given for the analysis of iridium-platinum alloys, metallic platinum and dental alloys, however, are quite modern, incorporating as they do the latest work of the American Bureau of Standards.

In the mercury chapter no reference is made to the determination as mercuric sulphide or as mercurous chloride or to the volumetric thiocyanate method, the separation of arsenic, antimony and tin by hydrogen sulphide in hydrochloric acid of different concentrations receives only a brief mention, and no really reliable process for separating selenium and tellurium is described, the cyanide method being, as stated, approximate only. The tin chapter has been enlarged by the addition of descriptions of the gravimetric determination of tin as stannic oxide, and of the zinc-zinc oxide and lime methods of decomposing cassiterite. The removal of ilmenite from tin ores by digestion with sulphuric acid is tedious, and a much more efficient cleaning of the ore can be obtained by fusion with bisulphate. Now that aluminium is one of the most important of the non-ferrous metals, it seems strange that the omission of any reference to the analysis of bauxite from the first edition has not been rectified in this volume. The analysis of aluminium alloys is, however, treated fairly fully and much better than in the first edition. The copper section is on the whole quite good, but surely it is time that the stannous chloride volumetric method disappeared from text-books on analysis.

The tungsten and molybdenum chapters are inadequate; an antiquated form of the *aqua regia* method of determining tungstic acid in ores is given, but Bullnheimer's method is given in detail, although it is questionable whether this clumsy method of doubtful accuracy is ever used nowadays. The addition of Cremer's method (persulphate fusion followed by precipitation with cinchonine) is hardly an improvement, especially as the meagre details given are actually misleading.

The description of Arnold's method for the analysis of tungsten powder is also too brief to be of much value. The procedures described for the determination of molybdenum in ores are all based on the same principle, namely, precipitation of the trisulphide by acidification of a thiomolybdate solution followed by ignition to the disulphide; neither the trioxide nor the lead molybdate method is mentioned, nor is pressure precipitation with hydrogen sulphide in acid solution as a means of separation from vanadium, which frequently is associated with wulfenite.

Dr. Schoeller has written the section on Metallic Salts which, though brief, contains adequate information on the properties and methods of analysing almost all the important inorganic salts which have an industrial use, with the exception of sodium sulphate, which was dealt with in volume I, and potassium salts which are discussed by Dr. J. T. Dunn in the succeeding section. This section, which is the shortest in the book, deals quite adequately with natural potash deposits and the various products obtained therefrom.

The fifth section is written by Dr. R. S. Morrell and Mr. W. E. Wornum. They classify the pigments by colours: white, grey, yellow, red, blue, violet, green, brown, black and bronze. The analysis of all the chief pigments of every colour is described, and special attention is paid to the detection of adulteration. Notes on the preparation and the fastness to light of most pigments are given. Among the newer pigments described are titanium white, "Timonox," and cadmium scarlets. One error only was noted in this section—the description of tungsten bronze as "sodium para-tungstate."

The final section by Dr. Morrell provides an account of the analysis of drying oils, thinners including recently introduced compounds such as hexalin, tetralin, etc., natural and synthetic balsams and resins, oil varnishes, black bituminous paints and varnishes, and cellulose ester varnishes and enamels.

The book will, no doubt, appeal to a large circle of chemists, but it is questionable whether it fills a real gap in chemical literature, for there are many text-books on the market covering in just as good, or a better manner, the ground dealt with in the individual sections, and it is a debatable point whether the grouping of all these subjects between one pair of covers is sufficiently attractive to the average chemist to justify him in paying the rather high price demanded, especially in these days of intensive specialisation.

A. R. POWELL.

COLLOID SYMPOSIUM MONOGRAPH. No. 6. Pp. 346. New York: The Chemical Catalog Company, Inc. 1928. Price \$6.50.

The appearance of the volume collecting the papers read at the annual Colloid Symposium in America is a matter of great interest to all advanced students of colloid chemistry. The present volume collects the papers read at the Sixth Colloid Symposium held at the University of Toronto, June 14, 15 and 16, 1928.

Twenty-five papers have been published, edited by Professor H. B. Weiser.

The first is the address given by Sir W. B. Hardy, who was the guest of honour. He outlines deep problems in his discussion on "Living Matter." The other papers are definite contributions to colloid chemistry based on experimental investigations.

Professor W. D. Harkins and his co-workers extend their survey of surface tension and adsorption phenomena. Special attention is paid to the ring method of determining surface tensions. A valuable inquiry is also made concerning the familiar Antonow rule, that "the interfacial tension between two liquids, mutually saturated with each other, is equal or very approximately equal to the difference between the surface tension of the two phases, each in contact with the vapour of the other phase." Practically all books on surface phenomena regard this rule as valid. Harkins now points out its limitations, and his results are of much importance.

Briggs follows with a paper on "Surface Conductance," showing that in aqueous solutions of low specific conductance present in the interstices of a diaphragm material, the electrical conductance through the interface phase is much greater than that through an equal volume of the liquid in bulk. Such conductance is not a function of the ζ potential. Possibly the method described may be utilised to obtain values of the relative specific surface areas, *i.e.* colloidalilty of materials.

Several authors deal with adsorption. Professor McBain and his associates discuss the "Adsorption of Sodium Oleate at the Air-Water Interface." The results are contrary to the prediction of the Gibbs theorem, and suggest that "the surface of a solution may be covered with a monomolecular film of adsorbed solute, but may also exhibit a high concentration of solute in the neighbourhood of the surface."

Professor Burton continues his work on the effect of temperature on the coagulation of copper solutions, whilst Stamm outlines 4 dynamic physical methods for revealing the structure of soft woods. There is practical value in this work.

Medical aspects are reflected in papers dealing with the fractionation of diphtheria antitoxic plasmas; the cataphoresis of blood cells and inert particles in sols and gels; methods of studying the surfaces of living cells and their relation to the phagocytosis of bacteria; and the rôle of haemoglobin in the blood.

Two accounts are given of investigations on emulsions: (1) The Effect of Emulsification in the Peptic Synthesis of Protein. (2) Emulsions and the Effect of Hydrogen-Ion Concentration upon their Stability. In the latter paper Krantz and Gordon support Fischer's hydrate theory in emulsions stabilised with gum tragacanth. Their use of the Donnan pipette for determining interfacial tensions is, however, open to serious objection. There follow two papers on rubber, one on organophilic colloids, and others dealing with gelatin systems, the technology of smokeless powder manufacture, catalysts, and photographic problems. Nichols gives a most important and highly interesting account of the development

by Svedberg and his pupils of the Ultra-centrifuge, and outlines the field of research opened by such an instrument.

The whole volume reflects the versatility of the colloid chemist, and indicates the rapid strides being made in *quantitative* research. The former purely descriptive aspect of colloid chemistry has now given way before the advances possible because of refined technique.

The Sixth Colloid Symposium Monograph is a credit to all concerned, including the publishers. It is a necessary addition to the bookshelf of the serious student of physical chemistry.

WILLIAM CLAYTON.

PRACTICAL PHYSIOLOGICAL CHEMISTRY. By S. W. COLE, M.A. Eighth edition. Pp. xii+481. Cambridge: W. Heffer & Sons. 1928. Price 16s.

When a book of this type reaches eight editions in twenty-four years, the present appearing only two years after the seventh, it is evident that it is accepted generally by the physiologist and the student as more than an ordinary standard text-book. The volume contains a large amount of theoretical instruction in chemistry, as well as practical exercises, since it is intended primarily for the medical student rather than for the chemist.

The analyst, who deals occasionally with blood or urine analysis, is almost sure to find all that he requires on these subjects, combined with an authoritative opinion as to the value of many of the tests described, and (at the same time) he will regret that it has not been possible to find room for a chapter on the examination of faeces. There are only one or two minor points on which he might join issue with Mr. Cole, as he may wonder why it is necessary in the determination of chlorides to ash gastric juice, but neither blood nor urine, where the titration is made direct. It is doubtful whether the benzidine test is the best for blood in urine, the reduced phenolphthalein test is surely more delicate; and, although lactose may appear in the urine of pregnant women, it should be mentioned that while a positive result probably indicates pregnancy, the absence of lactose does not exclude the possibility.

It is to be regretted that the calomel cell is considered so inaccurate and out of date that it is no longer worth a description, while a short account of the glass electrode would be useful.

Regarding the book as a whole, it is a pity that Mr. Cole did not take to heart the suggestion in the review of the seventh edition (ANALYST, 1926, 51, 273) that the proof reading should have been more thorough, as an otherwise excellent book is spoiled by misprints and misleading statements. On page 111 the student is instructed to dry a solution on a filter paper heated with boiling water, and on page 323 mention is made of "scraps of the precipitate," instead of "scrape off the precipitate." On p. 120 it would surely be advisable to clip^off the vacuum pump before letting in air to the distillation flask *via* the capillary, and for the same

experiment Mr. Cole gives two different figures, using the same series of letters in each figure, which is confusing. During the various editions of the book the author appears to have changed his allegiance from Duroglass to Pyrex ware, with the result that on p. 384 it is necessary to use a Duroglass flask for a Kjeldahl digestion, and two pages later one is advised to use a Pyrex flask for the same purpose. It would also appear unnecessary in these days to tell the student twice on a page, and about fifty times in the book, that the apparatus can be obtained from one particular firm of suppliers.

Referring to the estimation of acetone bodies in urine by Goldblatt's method, Mr. Cole tells us that it has only just been published, and that he has not had time to try it, but it is surely unnecessary to say this three years after its publication.

His bibliographical references are inconsistent, in that we get *Biochem. Journ.*, 19, 626 (1925)" and *Biochem. Journal*, VIII, p. 134"; sometimes they are included in the text in brackets and sometimes as footnotes.

In describing the degradation of starch the author appears to have attempted to combine old and new theories, with the result that he refers to amylo-amylose and amylo-dextrin, erythro-amylose and erythro-dextrin, and achroo-amylose and achroo-dextrin as separate entities.

The publishers have done well to issue a new edition of such a book at a reasonable figure.

T. McLACHLAN.

THE PROTAMINES AND HISTONES. By A. KOSSEL. Pp. 108. London: Longmans, Green & Co. 1928. Price 9s. net.

The late Professor Kossel devoted his scientific career to a study of the protamines and the histones. He was a pioneer in the investigation of these two groups and remained throughout his life the pre-eminent authority in the field of work. The results of a life-time of research were gathered together in this volume, which was completed only a few days before his death, and his book, a model of lucid handling of a complex subject, will undoubtedly remain for many years the standard text book of the subject with which it deals.

Kossel started his investigations of the protamines and histones from the biological aspect. He was first led to study the evolutionary changes which proteins undergo in the differentiation of the tissues. Those studies opened up an entirely new field of chemical investigation, and new methods of analysis had to be developed for the investigation of these newly recognised proteins. The general methods developed for the analysis of the material are firstly, the separation of the protamines from alcoholic solution as insoluble sulphates; secondly, the acid hydrolysis of the purified material and the separation of the basic from the non-basic constituents. The basic constituents are investigated by transformation into insoluble salts, and the non-basic by differential solubilities in various alcohols. The basic constituents of both protamines and histones consist entirely of one or

more of the di-amino acids—arginine, lysine or histidine; the non-basic constituents of mono-amino acids. In the endeavour to discover the methods by which the different units are linked into the molecule, considerable use has been made of the differential action of the proteolytic enzymes as an analytical tool.

The great interest of Kossel's work lies in the evidence which he brings forward that the proteins of the animal body are, in the biologically active tissues such as gland cells and generative cells, rebuilt to form histones and protamines, the latter group showing the greatest extent of reconstruction. In this reconstruction the mono-amino acids, found to such a large extent in the ordinary proteins of the cytoplasm, have been partially eliminated. These comparatively simple amino acids, which are without any strongly marked chemical individuality, doubtless assist in the building up of the colloidal character of the protein molecule, giving it a high degree of sensitiveness to physical changes in the environment. In cells showing great metabolic activity, such as gland cells and generative cells, maximum chemical activity and economy of space is obtained by the elimination of these amino acids and their replacement by others which possess highly individual chemical groupings, such as arginine with its guanidine grouping, histidine with the iminazole ring, and lysine with its terminal amino group. (It is interesting that cystine and tryptophane, both with a highly specialised structure, appear to be absent from both histones and protamines.) The result of this condensation is the production of bodies of a highly basic character, the basicity being due in some cases to the guanidine groups of arginine, in others to the terminal amino groups of lysine. In the living cell, the protamines and histones exist only in combination with nucleic acid, another body with a complex but precise constitution that is probably the index of a specialised chemical activity. It must remain for the present a subject of speculation as to how far the basic character of the protamines has been called into being by the acidic character of nucleic acid and *vice versa*, the biological functions of the active chemical groupings of both constituents of the nucleo-proteins remaining at present entirely unknown. Professor Kossel's book forms an indispensable guide to the methods that are available for further chemical investigation of the basic constituents.

D. JORDAN LLOYD.

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Obituary.

JOHN HOWARD BROWN JENKINS.

THE sudden death of John Howard Brown Jenkins at the Railway Clearing House on December 11th, while presiding at a meeting of railway officials, has deprived the chemical profession of a valued member, and those who had the privilege of his personal and intimate acquaintance of a very dear friend.

Mr. Jenkins was born in 1866, and in his early days was attracted to the science of engineering; in 1882 he commenced an apprenticeship at the Swindon works of the Great Western Railway under the late Mr. W. Dean, and in 1888 gained a Whitworth Exhibition. Later, he studied chemistry under the late F. W. Harris, F.I.C., in the Great Western Company's chemical laboratory; in 1892 he was appointed chemist to the Great Eastern Railway, and it was in this Company's laboratory at Stratford that he laid the foundations of the work which brought him to the notice of the industrial and engineering world. Subsequent to the grouping of the railways, he received the appointment of Chief Chemist to the London and North Eastern Railway, the position which he held at the time of his death.

His early engineering training assisted him in dealing with many of the problems he met with in the railway service, notably in the involved question of cylinders for compressed gases, on which he was regarded as an authority. In 1919 he became the Railway Companies' nominee to the Gas Cylinders Research Committee of the Department of Scientific and Industrial Research; on this Committee, he found his views in conflict with those of the majority, resulting in his issuing the Minority Report which accompanied the First Report of the Committee in 1921. Although his views were unacceptable to the majority of that

Committee, the sound basis and honesty of his opinions were freely admitted, and his report, even though it failed to gain support from any of his colleagues, was accepted by all as a valuable contribution to the knowledge of the subject. It is thought, by some, that certain aspects of the matter raised in the Minority Report may ultimately prove to be of much value in future developments. In further work he found his views to be in harmony with the whole Committee.

Mr. Jenkins' scientific and literary abilities found ample scope in the varied work of a railway chemist. He was a highly skilled metallographist, and contributed to the Society of Public Analysts in 1904, with Mr. D. G. Riddick, a valuable and beautifully illustrated paper on the Microscopic Examination of Metals. He also read before the Society in 1898 a paper on Japanese Wood Oil, and made many contributions to the discussions of papers on oils, waters, metals, etc. He was a Vice-President of the Society in 1915-16, and served on the Council during three separate periods. In 1897 he communicated to the Society of Chemical Industry papers on Hehner's Bromine Test for Oils and on Japanese Wood Oil, and in 1919 he wrote the Annual Report on Paints, Pigments, Varnishes and Resins for that Society. In 1923 he was elected a Fellow of the Institute of Chemistry.

His work as a railway chemist was well known to many chemists and manufacturers who had occasion to meet him at the Railway Clearing House and discuss matters connected with the packing and conveyance of ordinary and dangerous goods, but only those of his colleagues in close touch with his work know how valuable his help and advice were. All, however, who were associated with him in either capacity could not fail to recognise his unfailing courtesy and fairness. He was an indefatigable worker, a sound adviser, and a sincere friend, very modest and retiring, but tenacious to a degree of opinions he had formed and considered important. His kindly nature and humorous outlook, nevertheless, endeared him to those who differed from him, as well as those who agreed with him. He was a charming conversationalist and a remarkable correspondent. His death will be a great loss to the railway companies and the public for whom they cater. He leaves a widow and one son, who is a student at St. Thomas' Hospital Medical School.

L. ARCHBUTT.

Death.

We greatly regret to announce the death, on February 6th, of Mr. James West Knights, one of the oldest members of the Society. He was for 50 years Public Analyst for the County and Borough of Cambridge, Hunts., Wisbech, and King's Lynn.

The Fatty Acids and Component Glycerides of some New Zealand Butters.

By T. P. HILDITCH, D.Sc., F.I.C., AND EVELINE E. JONES, M.Sc.

(Read at the Meeting, February 6, 1929.)

WHEN a natural fat, composed of a mixture of neutral glycerides, is carefully oxidised in acetone solution with potassium permanganate, all the unsaturated groups present are broken down into mixtures of lower fatty acids and semi-acidic glyceride derivatives of azelaic acid, whilst fully-saturated triglycerides are left unaltered (Hilditch and Lea, *J. Chem. Soc.*, 1927, 3106; Collin and Hilditch, *J. Soc. Chem. Ind.*, 1928, 47, 261T). Consequently a natural mixture of fully-saturated and mixed saturated-unsaturated glycerides can be quantitatively resolved into a corresponding mixture of neutral and acidic products. This procedure not only leads to a simple method of ascertaining the proportion of fully-saturated glycerides in a fat, but, if they are present in reasonably large amounts, permits them to be isolated in quantity in the pure condition; analysis of the mixed fatty acids combined in the whole fat and in the fully-saturated portion by the methyl ester distillation method (*cf.* Collin and Hilditch, *loc. cit.*; Hilditch and Houlbrooke, *ANALYST*, 1928, 53, 246) then furnishes considerable information of a semi-quantitative nature with regard to the mode of union of the fatty acids with glycerol in the original fat.

This line of attack has been applied to the case of butter-fats, the materials selected for investigation being three bulk samples of ordinary deliveries of New Zealand butter. It was necessary, however, to devote considerable attention to the determination of the composition of the mixed fatty acids, since, as is well known, this is not an easy mixture to deal with on a quantitative basis. Indeed, the literature on the subject justifies this statement by its volume and also by the discrepant observations which it discloses. Whilst allowance should be made, especially in dealing with an animal fat (and perhaps above all with milk fats), for probable variations caused by differences in habit and feeding, it seems unlikely that these suffice always to account for the varying data which have been put forward from time to time; this view is perhaps confirmed by the fact that the characteristics which are the analyst's chief guide in the examination of butter (volatile soluble and insoluble acids, iodine value, saponification value, refractivity, etc.) have not been found subject to variations of by any means so wide an order.

THE DETERMINATION OF MIXED FATTY ACIDS BY FRACTIONAL DISTILLATION OF ESTERS.—It is probably unnecessary for the purpose of this communication to refer specifically to more than one or two of the more recent analyses of the mixed fatty acids of butter, commencing with that of Crowther and Hynd (*Biochem. J.*, 1917, 11, 139). These workers converted the mixed acids into methyl

esters and fractionally distilled the whole; the fact that even the lowest-boiling fractions contained some methyl oleate indicates that the fractionation method employed was not highly efficacious. Holland and Buckley (*J. Agric. Res.*, 1918, 12, 719), and subsequently Holland and co-workers (*ibid.*, 1923, 24, 365) have published data, obtained by somewhat similar methods, for a large number of butter-fats. The general results of both groups of workers were as follows:—

	Crowther and Hynd. Per Cent.	Holland and co-workers. Per Cent.
Butyric acid	4.6	2.2-4.2 ("by difference")
Caproic	1.7	1.3-2.4
Caprylic	1.3	0.5-1.0
Capric	1.3	1.2-2.0
Lauric	5.4	4.5-7.7
Myristic	17.7	15.6-22.6
Palmitic	16.0	5.8-22.9 ("by difference")
Stearic	3.7	7.8-20.4
Oleic	48.3	25.3-40.3

These results met with severe criticism from Channon, Drummond and Golding (*ANALYST*, 1924, 49, 311) and Elsdon (*ibid.*, 1924, 49, 423), mainly on the grounds that accuracy to the third place of decimals per cent. was apparently claimed and that the fractionation procedure had shown itself incapable of producing the binary mixtures of saturated esters necessary for arithmetical interpretation. Armstrong, Allan and Moore (*J. Soc. Chem. Ind.*, 1925, 44, 63T) emphasised the necessity for attention to certain vital points in connection with the preparation and fractionation of the esters (notably the isolation and characterisation of fractions of individual esters), and claimed that with due precautions an accuracy to within a unit per cent. was attainable.

We agree with the criticisms of the earlier attempts to apply the fractionation method quantitatively, and with Channon, Drummond and Golding in their statement that the procedure "can yield very valuable information if its limitations are recognised"; but we cannot go so far with these authors as to affirm that "as an exact quantitative method, it is of little value." Obviously, the strain upon the fractionation process should be lessened as much as possible by preliminary division of the acids into groups of varying character. Due attention to preliminary separations of this kind, coupled with precautions in the fractional distillation on the lines suggested by Armstrong, Allan and Moore, and subsequent workers, render an accuracy of within a unit per cent. quite attainable. This is shown by numerous results published from several independent sources within the past two or three years.

Whilst dealing with the fractionation method from a critical standpoint, two matters of detail may be mentioned:

(i) The isolation of absolutely individual esters, as postulated by Armstrong, Allan and Moore, is somewhat of a counsel of perfection when mixtures of small quantities of successive homologues are encountered; in such circumstances we prefer to collect a series of small fractions covering the region in which an individual member may be expected to predominate. This effectively minimises

any inaccuracy due to a possible error in the nature of the minor components of the mixture; the tables on pp. 80, 81 illustrate the general composition of final fractions as determined by our present method of operation.

(ii) It is our custom to collect the primary distillates in fractions as large as is consistent with the gradual rise in boiling-point and the general proportions of the mixture of esters known to be present. Each primary fraction is then submitted to refractionation as a separate entity; we do not in any circumstances add a subsequent primary fraction to the residue from the redistillation of its predecessor. This, in our opinion, makes the ultimate series of calculations more accurate, whilst it avoids the necessity for the employment of "corrected" weights in the latter.

In connection with the earlier data for the acids of butter-fat which we have discussed, we have a further criticism to make—all unsaturation seems to have been calculated on the assumption that oleic acid alone is present. The data which we give in this paper (*cf.* p. 84) show definitely that the unsaturated acids present contain small quantities of an acid less saturated than oleic. We have confirmed this by examination of the hydroxystearic acids prepared from the acids of the fractions concerned by alkaline permanganate oxidation, when, although we did not succeed in isolating any pure tetrahydroxystearic acid, the dihydroxystearic acid produced melted somewhat indefinitely about 5° below the true melting-point of 9, 10, dihydroxystearic acid from pure oleic acid. Further, a very small trace (insufficient for recrystallisation) of brominated acids insoluble in ether was obtained from the "liquid" fatty acids of the butter; this substance blackened, without definitely melting, at 170–180°. We conclude that the unsaturated acids of butter-fat (like those of most other fats) contain small proportions of linoleic acid and even traces of linolenic acid.

Allowance for this in the older analyses may reduce the proportion of unsaturated acids considerably in not a few cases (since, calculated on iodine value, two molecules of oleic acid appear as one of linoleic acid); consequently the amounts of some of the saturated acids will be correspondingly low.

In this connection, Holland's results with butter from cows fed on varying rations may be significant: the "oleic acid" figures, for example, for cows fed respectively on a general ration, on one including coconut oil, and on one including soya bean oil, were 30.8, 29.5 and 45.8 per cent., whilst the corresponding palmitic acid figures (determined "by difference") were 20.2, 17.1 and 8.7 per cent. It is quite possible that the apparent increase in "oleic acid" and the extremely low (differential) percentage of palmitic acid in the butter after diet including soya bean or other semi-drying oil, is really due in part to the presence of varying proportions of linoleic acid. We are proceeding with the investigation of butters from cows whose food has included different types of fatty material, and we hope thereby to throw further light on this matter.

As regards Holland and Buckley's figures for the volatile acids, it may be remarked that good agreement exists between these and the values obtained in

the present work, and also those arrived at recently by Virtanen and Pulkki (*Z. anal. Chem.*, 1928, **74**, 321) in the case of ten samples of Finnish butter. The latter included the following range: butyric acid, 3.1–4.2 per cent., and caproic acid, 1.4–2.1 per cent. It is permissible to conclude that the general proportions of the four lowest acids of butter are now known within comparatively narrow limits.

It has been said that, in the fractionation analysis of mixed fatty acids, each fatty mixture should be considered on the lines of a separate problem from the point of view of general procedure. As a rule, it is sufficient to effect a preliminary resolution by the lead-salt method into two groups:

(i) "Solid" acids containing all the stearic or higher acids, all but traces of palmitic, and most of the myristic and lower saturated acids, with small proportions of oleic acid;

(ii) "Liquid" acids containing all C_{18} acids less saturated than oleic, most of the oleic, minor amounts of myristic and lower saturated acids, but only traces of palmitic and no stearic or higher saturated acid.

The "volatile" acids of butter render this particular case more complicated.

We studied Crowther and Hynd's method in the first instance, and satisfied ourselves that the volatility of methyl butyrate rendered its application unsuitable, apart from the tendency, already discussed, for methyl oleate to distil to some extent throughout the process.

We have found it best to adopt, in effect, an intensive "Reichert-Meissl" procedure on a somewhat large scale. The fatty acids from 300–600 grms. of butter-fat are subjected to careful steam distillation for about four or five hours, *i.e.* sufficiently to ensure that the whole of the butyric and caproic acids have been removed. The acids volatile in steam are extracted by ether and fractionated as such, mainly at atmospheric pressure; the difference in boiling-point between the successive homologues is sufficient to permit binary mixtures to be separated. The extracted aqueous liquors and the recovered distilled ether are titrated with alkali, any acid present being calculated as butyric acid. The acids non-volatile in steam are recovered and weighed, and a suitable portion is submitted to the lead-salt separation, the resulting "solid" and "liquid" acids being converted into methyl esters and fractionated quantitatively in the usual way.

The satisfactory concordance which we have obtained by this procedure is not likely to be due merely to repetition of the same sequence of processes on similar materials by the same manipulator, since the following differences have been introduced:

(i) The determination of mixed fatty acids in the whole butter-fats "A" and "B" was carried out on about 600 grms. of each fat, and in "C" on 300 grms., whilst those of the fully-saturated glycerides of "A" were made on 200 grms., and of "B" on 140 grms. of material.

(ii) In the lead-salt separations of the acids non-volatile in steam, the "solid" acids in the case of "A" (56.7 per cent.) had an iodine value of 10.1 of "B" (67.5 per cent.), 23.2, and of "C" (54.4 per cent.), 11.8. Similarly, whilst the "liquid" acids of "A" and "B" (iodine values respectively 82.7 and 80.9) consisted of the corresponding soluble lead salts from the original separation united with the mother-liquors from the recrystallisation of the separated lead salts, in the case of "C," the acids from the soluble salts (38.4 per cent., iodine value 83.1) and from the mother-liquors from recrystallisation (7.2 per cent., iodine value 62.1) were methylated and fractionated separately.

DETERMINATION OF THE COMPOSITION OF THE FATTY ACIDS OF BUTTER-FAT.—The method adopted in these investigations will be illustrated by a detailed account of the experimental work on the New Zealand butter-fat "A."

The fat (approx. 600 grms.) was hydrolysed by prolonged boiling with excess of alcoholic caustic soda, after which as much alcohol as possible was removed from the soap by distillation. The flask containing the residual soap was then connected to a condenser for steam-distillation, an efficient spray-trap being inserted between the exit from the flask and the inlet to the condenser. In order to effect smooth distillation without frothing, it was found best first of all to remove residual alcohol from the soap by cautious steam-distillation; the soap solution was then cooled in the flask until it commenced to set to a jelly. At this point sufficient aqueous sulphuric acid was added to provide a slight excess of mineral acid after all the alkaline base present had been neutralised, and the fatty acids were then submitted to steam-distillation for about five hours; during this time about 5 litres of aqueous condensate was collected.

After cooling, the contents of the flask were extracted with ether, and from the washed ethereal solution the mixed non-volatile fatty acids were carefully recovered and weighed (551.1 grms., mean equivalent 259.9, iodine value 42.2); the quantitative analysis of the non-volatile acids is described below.

COMPOSITION OF STEAM-VOLATILE ACIDS.—The aqueous condensates were extracted five times with ether; the united extracts were dried over anhydrous sodium sulphate (which was subsequently washed with fresh dry ether to remove any adherent fatty acids), and the bulk of the ether was removed by distillation on the steam-bath. Portions of the ether-extracted aqueous solution (5345 c.c.) and of the recovered distilled ether (2394 c.c.) were titrated with standard alkali, and the acidity found calculated as *butyric acid* (2.10 grms. and 0.24 grm. in the respective liquids).

The remaining volatile acids were slowly distilled from a Willstätter fractionation bulb and collected in small fractions: the greater part of the distillation was carried out at atmospheric pressure, but a moderate (water-pump) vacuum was used in the final stages. The first four fractions contained (diminishing) quantities of ether and came over below the boiling point of *n*-butyric acid; the acid present in these was calculated as butyric, and that in the remaining fractions was calculated

from the mean equivalents on the assumption that only binary mixtures were present:

No.	Grms.	B.pt. °C.	Pressure.	Mean equivalent.	Butyric. Grms.	Caproic. Grms.	Caprylic. Grm.	Capric acids. Grm.	
	In aqueous solution				2.10				
	In recovered ether				0.24				
1	43.54	35/83	Atmospheric		0.97				
2	3.65	83/86			0.75				
3	1.96	88/156			1.69				
4	5.11	156/165			4.64				
5	6.30	165/170			95.4	4.27	2.03		
6	8.28	170/183	Reduced	97.8	4.84	3.44			
7	1.47	142/155			111.8	0.17	1.30		
8	4.23	155/167			119.0		3.68	0.55	
9	2.75	Residue			164.4			0.65	2.10
Totals:					19.57	10.45	1.20	2.10	

COMPOSITION OF ACIDS NON-VOLATILE IN STEAM.—A portion of the non-volatile acids (303 grms.) was treated with lead acetate (212 grms.) in boiling alcohol (2430 c.c.). The deposited lead salts were separated and recrystallised from an equal volume of alcohol. The recrystallised lead salts were re-converted into fatty acids (solid acids S, 170.3 grms.), whilst the alcoholic solutions were united and the dissolved lead salts contained therein also converted back to fatty acids (liquid acids L, 130.3 grms.):

	Per Cent.	Present in 551.1 grms.	Mean equivalent.	Iodine value.
Solid acids S	56.7	312.2	259.2	101.5
Liquid acids L	43.3	238.9	257.3	82.7

Each group of acids was converted into neutral methyl esters, and these were fractionally distilled in the usual way from a Willstätter bulb under high vacuum; in both cases it was only necessary to re-fractionate the first fraction:

METHYL ESTERS OF SOLID ACIDS S.

Primary fractionation.					Refractionation.				
No.	Grms.	B.pt./ 1 mm. °C.	Saponi- fication equivalent.	Iodine value.	No.	Grms.	B.pt./ 1 mm. °C.	Saponi- fication equivalent.	Iodine value.
S1	52.71	70-130	254.2	2.6	S11	0.79	86-105	217.5	—
					S12	1.44	105-115	231.6	—
					S13	5.45	115-120	242.0	—
					S14	9.94	120-123	248.2	1.2
					S15	11.23	123-130	255.5	1.2
S2	48.07	130-132	273.2	6.2	S16	4.63	130-132	264.1	1.9
					S17	9.39	132-135	270.2	2.7
					S18	5.71	Residue	277.5	9.8
					48.58				
S3	13.01	132-135	280.6	12.0					
S4	13.22	135-136	287.6	18.0					
S5	21.14	136-144	294.6	22.0					
S6	8.84	144-148	296.4	21.5					
S7	7.62	Residue	305.0	20.6					
164.61									

METHYL ESTERS OF LIQUID ACIDS L.

Primary fractionation.					Refractionation.				
No.	Grms.	B.pt./ 1 mm. °C.	Saponi- fication equivalent.	Iodine value.	No.	Grms.	B.pt./ 1 mm. °C.	Saponi- fication equivalent.	Iodine value.
L1	33.51	44-130	232.8	34.1	L11	0.64	39-50	161.4	8.6
					L12	1.06	50-66	171.8	8.6
					L13	2.34	66-69	186.4	14.2
					L14	2.84	69-92	198.2	12.5
					L15	3.57	92-105	217.2	12.1
					L16	4.48	105-114	236.2	22.7
					L17	5.20	114-115	243.5	26.0
					L18	9.52	Residue	275.4	67.7
						29.65			
L2	16.55	130-140	288.0	76.2					
L3	40.91	140-150	296.3	96.8					
L4	12.67	150-152	297.7	98.0					
L5	11.44	152-155	296.6	99.8					
L6	8.99	Residue	325.5	108.4					

124.07

The primary residues were saponified, and any unsaponifiable matter present extracted by means of ether from the aqueous solution of the potassium salts. The fatty acids, freed from unsaponifiable matter, were recovered, and their equivalents and iodine values re-determined. These figures, which are more accurate than those for the small proportions of unsaponifiable matter present, have been employed in calculating the amount of the latter.

The amounts of each ester present can now be calculated (in the esters of liquid acids L the assumption is made that the unsaturated C_{18} esters present in L1 and L2 had the same relative composition as the first pure C_{18} ester fraction, *i.e.* possessed an iodine value of 96.8).

METHYL ESTERS OF SOLID ACIDS S.

	S11.	S12.	S13.	S14.	S15.	S16.	S17.	S18.	Total.	Per cent. as esters.	Per cent. as fatty acids.
	Grms.	Grms.	Grms.	Grms.	Grms.	Grms.	Grms.	Grms.	Grms.		
Laurate	0.68	0.49	—	—	—	—	—	—	1.17	2.4	
Myristate	0.11	0.95	5.45	7.66	5.63	0.97	0.15	—	20.92	43.1	
Palmitate	—	—	—	2.14	5.44	3.56	8.95	4.01	24.10	49.6	
Stearate	—	—	—	—	—	—	—	1.05	1.05	2.2	
Oleate	—	—	—	0.14	0.16	0.10	0.29	0.65	1.34	2.7	

	S1	S2.	S3.	S4.	S5.	S6.	S7.			
Laurate	1.27	—	—	—	—	—	—	1.27	0.8	0.8
Myristate	22.70	—	—	—	—	—	—	22.70	13.8	13.7
Palmitate	26.15	41.63	7.64	4.45	2.01	0.30	—	33.13	49.9	49.9
Stearate	1.14	2.96	3.55	4.00	13.70	6.33	3.60	37.28	23.7	23.8
Arachidate	—	—	—	—	—	—	2.19	2.19	1.3	1.3
Oleate	1.45	3.48	1.82	2.77	5.43	2.21	1.83	18.99	11.5	11.5

METHYL ESTERS OF LIQUID ACIDS L.

	L11.	L12.	L13.	L14.	L15.	L16.	L17.	L18.	Total.	Per cent. as esters.	Per cent. as fatty acids.
	Grms.	Grms.	Grms.	Grms.	Grms.	Grms.	Grms.	Grms.	Grms.		
Caproate	0.08	—	—	—	—	—	—	—	0.08	0.3	
Caprylate	0.50	0.67	0.67	—	—	—	—	—	1.84	6.2	
Caprate	—	0.30	1.33	2.20	0.49	—	—	—	4.32	14.6	
Laurate	—	—	—	0.27	2.63	2.30	1.72	0.44	7.36	24.8	
Myristate	—	—	—	—	—	1.13	2.08	2.43	5.64	19.0	
Oleate	0.05	0.08	0.30	0.32	0.39	0.92	1.22	5.81	9.09	30.7	
Linoleate	0.01	0.01	0.04	0.05	0.06	0.13	0.18	0.84	1.32	4.4	

	L1.	L2.	L3.	L4.	L5.	L6.			
Caproate	0.09	—	—	—	—	—	0.09	0.1	0.1
Caprylate	2.08	—	—	—	—	—	2.08	1.7	1.6
Caprate	4.88	—	—	—	—	—	4.88	3.9	3.8
Laurate	8.32	—	—	—	—	—	8.32	6.7	6.6
Myristate	6.37	0.94	—	—	—	—	7.31	5.9	5.9
Palmitate	—	2.48	—	—	—	—	2.48	2.0	2.0
Oleate	10.28	11.38	35.74	10.89	9.60	6.87	84.76	68.3	68.6
Linoleate	1.49	1.65	5.17	1.78	1.84	1.31	13.24	10.7	10.7
Unaponifiable	—	—	—	—	—	0.81	0.81	0.7	0.7

The whole of the experimental data for the original mixed fatty acids are then combined as follows:

NEW ZEALAND BUTTER-FAT "A."

Acid.	Acids non-volatile in steam.			Total. Grms.	Per cent. excluding unsaponi- fiable matter.
	Volatile acids. Grms.	Solid acids S. Grms.	Liquid acids L. Grms.		
	33.32	312.3	238.8	584.42	
Butyric ..	19.57	—	—	19.57	3.4
Caproic ..	10.45	—	0.16	10.61	1.8
Caprylic ..	1.20	—	3.85	5.05	0.9
Capric ..	2.10	—	9.16	11.26	1.9
Lauric ..	—	2.37	15.78	18.15	3.1
Myristic ..	—	42.77	13.97	56.74	9.7
Palmitic ..	—	155.80	4.77	160.57	27.6
Stearic ..	—	71.04	—	71.04	12.2
Arachidic (?) ..	—	4.14	—	4.14	0.7
Oleic ..	—	36.18	163.87	200.05	34.3
Linoleic ..	—	—	25.60	25.60	4.4
(Unaponifiable) ..	—	—	1.64	1.64	—

The New Zealand butter-fats "B" and "C" were investigated by the same method, except that in the case of "C" the quantity of fat employed was only about half of that used in the other instances. The final results are given in the next tables:

NEW ZEALAND BUTTER-FAT "B."

Acid.	Acids non-volatile in steam.				Per cent. (excluding unsaponifiable matter).
	Volatile acids. Grms.	Solid acids S. Grms.	Liquid acids L. Grms.	Total. Grms.	
	32.71	369.2	178.2	580.11	
Butyric	18.09	—	—	18.09	3.1
Caproic	11.07	—	—	11.07	1.9
Caprylic	0.85	—	3.73	4.58	0.8
Capric	2.70	1.10	7.71	11.51	2.0
Lauric	—	7.82	14.93	22.75	3.9
Myristic	—	48.85	12.23	61.08	10.6
Palmitic	—	162.54	0.14	162.68	28.1
Stearic	—	49.12	—	49.12	8.5
Arachidic (?)	—	5.60	—	5.60	1.0
Oleic	—	94.17	116.73	210.90	36.4
Linoleic	—	—	21.39	21.39	3.7
(Unsaponifiable)	—	—	1.34	1.34	—

NEW ZEALAND BUTTER-FAT "C."

Acid.	Acids non-volatile in steam.				Per cent. (excluding unsaponifiable matter).
	Volatile acids. Grms.	Solid acids S. Grms.	Liquid acids L. Grms.	Total. Grms.	
	17.05	162.8	136.3	316.15	
Butyric ..	10.11	—	—	10.11	3.2
Caproic ..	5.24	—	—	5.24	1.7
Caprylic ..	0.93	—	1.73	2.66	0.8
Capric ..	0.32	—	6.86	7.18	2.3
Lauric ..	0.45	1.60	11.46	13.51	4.3
Myristic ..	—	20.10	13.83	33.93	10.8
Palmitic ..	—	88.95	0.53	89.49	28.4
Stearic ..	—	29.50	—	29.50	9.4
Arachidic (?) ..	—	2.50	—	2.50	0.5
Oleic ..	—	20.14	84.11	104.25	33.1
Linoleic ..	—	—	16.81	16.81	5.4
(Unsaponifiable) ..	—	—	0.97	0.97	—

In the next table are collected the characteristics of each of the butter-fats, together with the final results of the fractionation analyses, and the equivalents and iodine values of the mixed fatty acids and fats calculated from the latter figures:

MIXED FATTY ACIDS OF NEW ZEALAND BUTTERS.

						"A"	"B"	"C"
BUTTER-FAT:								
Sap. Equiv.	247.5	250.7	249.5
Iodine value	38.0	39.4	39.3
Reichert-Meissl value	28.4	25.8	25.4
Polenske value	1.9	2.3	2.1
Kirschner value	23.7	20.9	20.3
Butyric acid (calculated from Kirschner value)	4.2	3.7	3.6

ACIDS BY FRACTIONATION ANALYSIS:							"A"	"B"	"C"
							Per Cent.	Per Cent.	Per Cent.
Butyric	3.4	3.1	3.2
Caproic	1.8	1.9	1.7
Caprylic	0.9	0.8	0.8
Capric	1.9	2.0	2.3
Lauric	3.1	3.9	4.3
Myristic	9.7	10.6	10.8
Palmitic	27.6	28.1	28.4
Stearic	12.2	8.5	9.4
Arachidic (?)	0.7	1.0	0.5
Oleic	34.3	36.4	33.1
Linoleic	4.4	3.7	5.4

CALCULATED MEAN VALUES (from fractionation analyses):

Sap. equiv.	Fatty acids	238.2	238.0	237.8
	Glycerides	250.9	250.7	250.5
Iodine value.	Fatty acids	38.9	39.5	39.6
	Glycerides	36.9	37.5	37.6

Consideration of these figures should be prefaced by a word as to the limits of accuracy, qualitative and quantitative, of our experiments. Since the majority of the fatty acids of butter have been definitely recognised for many years, we have only formally identified our products in certain cases. We may point out, in passing, that individual esters, when predominating in the distillates, were readily recognised by their boiling-points at the pressure employed, and that, in particular, the greater part of the methyl palmitate present was obtained in fractions in which it was the main component and which crystallised in the well-defined form characteristic of this ester. Methyl stearate was also definitely recognised, both as ester and in the form of stearic acid isolated therefrom.

The small proportions of fatty acid calculated as "arachidic" represent increments of a fatty acid of higher molecular weight than stearic (calculated after elimination of any accompanying unsaponifiable matter); the amount present was so small that it was not possible to obtain any fraction rich in this material, and we have not therefore been able positively to identify it. In these circumstances we have calculated it in terms of the next even-member acid higher in the series than stearic, *i.e.* as arachidic acid. The error, if any, is small, owing to the minor amount present.

With reference to the linoleic acid content of butter-fat, we would point out that the presence of an acid more unsaturated than oleic is consistently borne out by the iodine values of the C_{18} unsaturated esters obtained in fractionation of the liquid acids (*cf.* pp. 81, 83). The major C_{18} liquid ester fractions from the respective butters possessed the following characteristics:

	Sap. equiv.	Iodine value.
"A"	296.3	96.8
"B"	293.6	99.3
"C"	293.5	97.2

We experienced more difficulty than had been anticipated in preserving the freshly-distilled unsaturated C_{18} esters from atmospheric oxidation, and it is consequently probable that the figures for linoleic acid are, if anything, on the low side

(especially in butter-fat "B"). Absorption of oxygen and diminution in iodine value set in rapidly when these esters are stored, and we have adopted the practice of placing such fractions in rubber-stoppered bottles in an atmosphere free from oxygen immediately they have been collected.

A comparison of the data obtained (*cf.* table, pp. 83, 84) shows that the mean equivalents of the mixed fatty acids, recalculated from the fractionation data, correspond fairly closely with those of the original fats, whilst the calculated iodine values are slightly, but consistently, low, probably for the reason just stated.

As regards the figures for individual acids, it appears probable from the results for "B" and "C" (two almost identical fats) that the mean error is only a few tenths per cent. except in the case of the saturated acids of highest molecular weight and the unsaturated acids. It may be repeated that we believe that this method of analysis is reliable to the nearest whole number (per cent.) (*cf.* ANALYST, 1927, 52, 253), and we are disinclined to lay much stress on fractional values. Nevertheless, in the case of butter-fats the small proportions of the lower acids present unfortunately render this course necessary to some extent.

The data for butyric-capric acids, however, are concordant in their relationship to the observed Kirschner values, and are also within the comparatively narrow range for each acid assigned by Holland and Buckley (*loc. cit.*).

The relation of the observed butyric acid content to that calculated on the assumption that the Kirschner value is a simple measure of butyric acid would seem to show that the latter registers, in terms of butyric acid, about 15–20 per cent. more than is actually present in the fat.

The unsaturated acids present are very similar in composition to those present in tallow, and consist of oleic acid admixed with about 12–15 per cent. of linoleic acid; the total unsaturated acid content of the mixed fatty acids now studied was 38.5–41 per cent.

The data for the higher saturated fatty acids, in which so much variation occurs in the earlier literature, are consistent in showing a content of 9.7–10.8 per cent. of myristic, and 27.6–28.4 per cent. of palmitic acid; whilst the observed values for stearic acid are 8.5, 9.4 and 12.2 per cent. We believe that the analyses establish palmitic acid as the predominating saturated component of these butter fatty acids, whilst they also show that myristic and stearic acids are each present to the extent of rather more than one-third of the weight of palmitic acid.

Mitchell (ANALYST, 1924, 49, 515) has recently obtained figures from which he concludes that the stearic acid content of butter-fats may range from practically nothing to 22 per cent. at least. It is noteworthy that in the three samples now examined, all otherwise closely similar, there is a wider variation in the stearic acid figures than in those of any of the other saturated acids.

From the fundamental standpoint it is perhaps more important to compare the *relative molecular quantities* of the acids combined in a natural fat, and therefore it is interesting to tabulate the number of equivalents of each fatty acid present in the three butter-fats and in tallow; for this purpose we have employed figures for a mutton tallow recently obtained in this laboratory, and for an Australian

beef tallow as recorded by Armstrong and Allan (*J. Soc. Chem. Ind.*, 1924, **43**, 216T):

Acid.	Australian beef tallow.	Mutton tallow.
	Per Cent.	Per Cent.
Myristic ..	2.0	4.6
Palmitic ..	26.5	24.6
Stearic ..	22.5	30.5
Oleic ..	49.0	36.0
Linoleic ..	—	4.3

Composition of Fatty Acids in Equivalents (per cent.).

Acid.	New Zealand Butter-fats.			Tallows.	
	A.	B.	C.	Australian beef.	Mutton.
Butyric	9.2	8.4	8.7	—	—
Caproic	3.7	3.9	3.4	—	—
Caprylic	1.4	1.3	1.4	—	—
Capric	2.7	2.8	3.1	—	—
Lauric	3.7	4.6	5.1	—	—
Myristic	10.2	11.0	11.2	2.4	5.4
Palmitic	25.7	26.2	26.3	28.3	26.3
Stearic	10.2	7.1	7.8	21.7	29.3
Arachidic	0.5	0.8	0.6	—	—
Oleic and linoleic	32.7	33.9	32.4	47.6	39.0

The following points may be noted:

(i) One hundred molecules of the mixed fatty acids include in all cases about 26 molecules of palmitic acid (how far this is a general rule in the case of tallows is of course uncertain; the average of four other available analyses of tallows, however, shows 27.6 mols. of palmitic acid per 100 mols. of mixed fatty acids).

(ii) The presence of the fatty acids lower than palmitic in butter-fat is balanced by a lower molecular content of C_{18} acids, as compared with the tallows—the palmitic acid figure remaining about the same.

(iii) About one-third of the molecules of the mixed fatty acids of the butters are those of oleic and linoleic acids.

(iv) Butyric, myristic and stearic acids are present in something approximating to equimolecular proportions in the butter-fats examined.

(v) The six lowest-molecular-weight acids of the butter-fats can be arranged as follows in pairs which correspond, roughly, in their respective molecular proportions:

Butyric (C_4), 8.4–9.2 per cent., and myristic (C_{14}), 10.2–11.2 per cent.

Caproic (C_6), 3.4–3.9 per cent., and lauric (C_{12}), 3.7–5.1 per cent.

Caprylic (C_8), 1.3–1.4 per cent., and capric (C_{10}), 2.7–3.1 per cent.

The circumstance that this approximate relationship may subsist between pairs of acids which respectively make up unit groups of 18 carbon atoms, together with the comparative deficiency of butter-fat in stearic acid as compared with

tallow, may not be without significance from a biochemical standpoint; but we hesitate, in the absence of a much wider series of analyses, to do more than draw attention to what is, perhaps, only a coincidence.

INVESTIGATION OF THE COMPONENT GLYCERIDES OF BUTTER-FAT.—As already stated, the procedure adopted has been to oxidise butter-fat until all unsaturated linkages have been converted into free acidic groups, leaving only the original fully-saturated glycerides in the form of neutral compounds. The latter have then been freed as completely as possible from acidic products of oxidation, and their weight noted; after which the composition of their mixed fatty acids has been determined precisely as in the case of the original butter-fat, except that, of course, the lead-salt separation has been omitted, unsaturated acids now being absent.

The distribution of the acids in the fully-saturated and the mixed saturated-unsaturated glycerides has then been arrived at by comparison with the analytical data for the original butter-fats: direct analysis of the fatty acids in the acidic oxidation products is impracticable owing to the impossibility at present of effecting quantitative removal of nonoic acid (one of the free acidic products) without concurrent decomposition of the acidic glyceride compounds.

Butter-fats "A" and "B" have been submitted to this treatment, which will be briefly described before summarising the analytical figures which have been obtained.

The fat (1 part) was dissolved in acetone (10 parts), and powdered potassium permanganate (4 parts) was added in small quantities at a time (with vigorous shaking at each addition), while the solution was gently boiled under a reflux condenser; boiling was continued for a short time after addition of the oxidant had been completed, after which as much acetone as possible was removed by distillation and treatment of the residue at 90–100° C. under reduced pressure. In order to minimise any chance of glyceride-hydrolysis in the alkaline solution (by potassium hydroxide possibly liberated from the permanganate), the resulting friable powder was mixed with powdered sodium bisulphite, and then with water; the aqueous mixture was warmed and cautiously decolorised by the gradual addition of dilute sulphuric acid with vigorous stirring; after cooling, the solution was thoroughly extracted with ether.

The united ethereal extracts, after washing with water, were shaken repeatedly with small quantities of dilute ammonia, followed (when the whole was definitely alkaline) by thorough washing with water to remove as much of the organic ammonium salts as possible. The ammoniacal and aqueous liquors were re-extracted with ether to remove any neutral glycerides present in the emulsified condition, and all the ethereal extracts were then concentrated and the residual neutral product dried.

If the iodine value of the neutral product was appreciable (*e.g.* above 0.5), the material was submitted to a repetition of the oxidation process. Eventually, crude neutral products with an iodine value of 0.3 or less were obtained; in this

condition, however, they still possessed a small acid value due to the retention of traces of the difficultly-removable acidic glyceride compounds (*e.g.* of the type $C_3H_5(O.CO.R)_2(O.CO.[CH_2]_7.COOH)$, where R represents a higher saturated fatty acid radicle).

They were therefore boiled in water to which dilute sodium carbonate was added until the whole was definitely alkaline to phenolphthalein. The aqueous layer (containing some emulsified neutral glycerides) was separated from the main fatty portion, which formed a clear upper layer; the latter was boiled several times with water until the washings remained neutral. By this means 80 to 90 per cent. of the crude neutral product was obtained in the form of material of negligible acid value, whilst ether-extraction of the united alkaline and aqueous wash-liquors furnished the remainder (10–15 per cent. of the whole) as a substance which still possessed a definite, though low, acid value. This acidity has been allowed for by assuming that it is due to the presence of acidic compounds of the same order as those removed by the sodium carbonate from the crude product (the free acidic compounds from the extracted alkaline wash-liquors having been isolated and their acid value determined).

The data thus obtained are sufficient to determine the proportion of fully-saturated glycerides present (to within one per cent.), and it then only remains to accumulate sufficient of these (a minimum of 150 grms. is desirable) for accurate determination of their fatty acid composition according to the scheme given on pp. 78–82.

FULLY-SATURATED GLYCERIDES OF BUTTER-FAT "A."—The fat yielded, as a result of complete oxidation, 33.6 per cent. of crude neutral products; oxidations were conducted on six batches of 100 grms. each, in order to provide sufficient material for detailed analysis.

On boiling the crude neutral product with dilute sodium carbonate, as described above, there were obtained:

- (a) 163.8 grms. completely neutral fat, sap. equiv. 229.3 (acid value 0.4);
- (b) 22.9 grms. fat extracted by ether, sap. equiv. 234.1 (acid value 6.4);
- (c) 12.5 grms. acidic material, sap. equiv. 167.9 (acid value 211.2).

Assuming that the acidic matter present in (b) has the same acid value as (c), the proportion of fully-saturated glycerides in the original fat is

$$\frac{33.6}{199.2} \left(163.8 + \frac{22.9 \times 204.8}{211.2} \right) = 31.3 \text{ per cent.}$$

The value 31 per cent. of fully-saturated glycerides in butter-fat "A" has been used in the subsequent calculations.

COMPOSITION OF THE FATTY ACIDS PRESENT IN THE FULLY-SATURATED
GLYCERIDES OF BUTTER-FAT "A."

Analysis of the combined neutral products (a) and (b) gave results which are summed up in the following table :

Acid.	Volatile acids. Grms.	Acids non-volatile in steam. Grms.	Total. Grms.	Per cent. (excluding unsaponi- fiable matter).
	14.77	157.37	172.14	
Butyric	7.50	—	7.50	4.4
Caproic	5.79	—	5.79	3.4
Caprylic	0.75	1.37	2.12	1.2
Capric	0.62	3.83	4.45	2.6
Lauric	0.11	6.26	6.37	3.7
Myristic	—	31.76	31.76	18.5
Palmitic	—	78.78	78.78	45.9
Stearic	—	34.99	34.99	20.3
(Unsaponifiable) ..	—	0.38	0.38	—

FULLY-SATURATED GLYCERIDES OF BUTTER-FAT "B."—After complete oxidation the original fat yielded 33.5 per cent. of crude neutral products, which on boiling with dilute sodium carbonate gave:

- (a) 134.6 grms. completely neutral fat sap. equiv. 232.5 (acid value 0.3);
- (b) 9.5 grms. fat extracted by ether, sap. equiv. 232.2 (acid value 15.4);
- (c) 19.3 grms. acidic material, sap. equiv. 193.6 (acid value 104.9).

The proportion of fully-saturated glycerides is therefore

$$\frac{33.5}{163.4} \left(134.6 + \frac{9.5 \times 89.5}{104.9} \right) = 29.2 \text{ per cent.}$$

The value 29 per cent. of fully-saturated glycerides in butter-fat "B" has been used in subsequent calculations.

COMPOSITION OF THE FATTY ACIDS PRESENT IN THE FULLY-SATURATED
GLYCERIDES OF BUTTER-FAT "B."

The final results of this analysis are summarised in the next table.

Acid.	Volatile acids. Grms.	Acids non-volatile in steam. Grms.	Total. Grms.	Per cent. (excluding unsaponi- fiable matter).
	12.2	115.3	127.5	
Butyric	5.35	—	5.35	4.2
Caproic	3.35	—	3.35	2.6
Caprylic	3.50*	0.77	4.27	3.3
Capric	—	3.04	3.04	2.4
Lauric	—	5.54	5.54	4.3
Myristic	—	22.44	22.44	17.6
Palmitic	—	58.25	58.25	45.7
Stearic	—	24.93	24.93	19.6
Arachidic	—	0.33	0.33	0.3

* This figure is almost certainly high at the expense of correspondingly low values for caproic and capric acids, owing to an unfortunately incomplete separation at the close of the fractional distillation of the volatile acids in this analysis.

DISTRIBUTION OF THE FATTY ACIDS IN THE GLYCERIDES OF BUTTER-FAT.—The next tables show the general composition of 100 parts of the glycerides of butter-fats "A" and "B," as indicated by the foregoing analyses.

BUTTER-FAT "A."

			Original fat. 100	Fully- saturated glycerides. 31	Mixed saturated- unsaturated glycerides (by difference). 69	
Glycerol residue	5.1	1.7	3.4	
						(Molecular ratios).
Butyric acid	3.2	1.3	1.9	22
Caproic	1.7	1.0	0.7	6
Caprylic	0.9	0.3	0.6	3
Capric	1.8	0.8	1.0	6
Lauric	2.9	1.1	1.8	9
Myristic	9.2	5.4	3.8	17
Palmitic	26.2	13.4	12.8	50
Stearic	11.6	6.0	5.6	20
Arachidic	0.7	—	0.7	2
Oleic	32.5	—	32.5	115
Linoleic	4.2	—	4.2	15

BUTTER-FAT "B."

			Original fat. 100	Fully- saturated glycerides. 29	Mixed saturated- unsaturated glycerides (by difference). 71	
Glycerol residue	5.1	1.6	3.5	
						(Molecular ratios).
Butyric acid	2.9	1.1	1.8	20
Caproic	1.8	0.7	1.1	9
Caprylic	0.8	0.9*	(-0.1)	—
Capric	1.9	0.7	1.2	7
Lauric	3.7	1.2	2.5	13
Myristic	10.0	4.8	5.2	23
Palmitic	26.6	12.5	14.1	55
Stearic	8.1	5.4	2.7	9
Arachidic	1.0	0.1	0.9	3
Oleic	34.6	—	34.6	123
Linoleic	3.5	—	3.5	12

* This figure is almost certainly high, cf. footnote to Table, p. 89.

On the whole, the series of analyses for the two fats (which, it will be remembered, differ mainly in that "A" has somewhat higher Reichert-Meissl and Kirschner values than "B") are in fair accordance and show clearly:

(a) That the proportion of fully-saturated glycerides in these fats is of the order of 30 per cent.;

(b) That all the saturated acids are distributed more or less evenly throughout both the fully-saturated and the mixed saturated-unsaturated parts of the fat. Recent work on the Reichert-Meissl, Kirschner, iodine and other values of fractions of Irish butter-fat separated by chilling at various temperatures has led Arup (ANALYST, 1928, 53, 641) to a similar conclusion.

The general distribution of the saturated fatty acids is made clearer by comparing the proportions of these acids present in the whole fat, the fully-saturated part, and the mixed saturated-unsaturated part. The tables which follow give these data for each fat both in the form of weight-percentages and of molecular percentages (the proportionate numbers of *equivalents* of each acid present).

RELATIVE COMPOSITION OF THE SATURATED FATTY ACIDS.

(i) WEIGHT PERCENTAGES.

Acid.	Butter-fat "A."			Butter-fat "B."		
	Whole fat.	Fully-saturated part.	Mixed saturated-unsaturated part.	Whole fat.	Fully-saturated part.	Mixed saturated-unsaturated part.
Butyric	5.5	4.4	6.7	5.2	4.2	6.1
Caproic	2.9	3.4	2.5	3.2	2.6	3.7
Caprylic	1.5	1.2	1.7	1.3	3.3*	—*
Capric	3.1	2.6	3.6	3.3	2.4	4.2
Lauric	5.1	3.7	6.4	6.5	4.3	8.5
Myristic	15.8	18.5	13.1	17.7	17.6	17.7
Palmitic	45.0	45.9	44.3	46.9	45.7	47.8
Stearic	19.9	20.3	19.4	14.2	19.6	9.0
Arachidic	1.2	—	2.3	1.7	0.3	3.0

(ii) MOLECULAR PERCENTAGES.

Acid.	Butter-fat "A."			Butter-fat "B."		
	Whole fat.	Fully-saturated part.	Mixed saturated-unsaturated part.	Whole fat.	Fully-saturated part.	Mixed saturated-unsaturated part.
Butyric	13.6	11.0	16.2	12.7	10.5	14.6
Caproic	5.4	6.5	4.6	6.0	4.9	6.7
Caprylic	2.3	1.8	2.5	1.9	5.0*	—*
Capric	3.9	3.3	4.5	4.1	3.1	5.2
Lauric	5.5	4.1	6.8	7.0	4.7	9.0
Myristic	15.0	17.9	12.3	16.8	17.0	16.4
Palmitic	38.2	39.6	36.9	39.5	39.3	39.4
Stearic	15.2	15.8	14.6	10.8	15.2	6.7
Arachidic	0.9	—	1.6	1.2	0.3	2.0

* Cf. footnotes to Tables on pp. 89, 90.

Bearing in mind the undesirability of attaching too great importance to the values for caproic-lauric acids (which are present in amounts too small for accurate determination by the methods employed), it nevertheless appears that there is a definite, though slight, tendency for the lower fatty acids to associate with the unsaturated fatty acids more than with the higher saturated acids. This is compensated for by a slight corresponding concentration of myristic, palmitic

and stearic acids in the fully-saturated glycerides; but it is noteworthy that the relative proportions of palmitic acid vary less than those of the other acids. Palmitic acid, indeed, appears to stand somewhat apart in its general relationships from the other acids throughout the whole series of analyses—a feature which we believe is characteristic of this acid in many other fats of vegetable, as well as animal origin.

We have not yet attempted to separate the fully-saturated glycerides by selective crystallisation from an appropriate solvent, but their free solubility in ether and acetone leads us to believe that they consist of a complex system of mixed glycerides, and to share the view of other workers that simple triglycerides are not present; from the general characteristics and properties of the material it does not appear probable, moreover, that glycerides containing only palmitic and stearic acids are present in any notable proportion.

COMPOSITION OF THE MIXED SATURATED AND UNSATURATED GLYCERIDES.—

The numerical data which we have obtained permit us to estimate the relative molecular proportions of saturated and unsaturated fatty acids combined in this section of the fat, and therefrom to give certain limiting figures for the amounts of mono-oleo- and di-oleo- glycerides and of triolein which may be present (in discussing this aspect of the results, the unsaturated matter is referred to for simplicity as though it were all made up of oleic acid). It would be possible to assign definite values to each of these three groups if, for example, we were able to obtain an independent figure for the percentage of triolein present; but our attempts to devise a procedure to this end have hitherto been unsuccessful.

We have two almost independent methods available for determining the molecular ratio of saturated and unsaturated acids combined in the mixed saturated-unsaturated glycerides of the fat:

(i) Given the percentage of fully-saturated glycerides present, the mean equivalents of these and of the original fat, and the proportion of saturated acids in the original fat, the mean equivalent, x , of the saturated acids linked with unsaturated acids in mixed glycerides can be directly obtained, and hence the molecular ratio of the saturated and unsaturated acids:

$$\frac{\text{Acids in 100 grms. fat}}{\text{Mean equivalent of total fatty acids.}} = \frac{\text{Acids in fully-saturated part}}{\text{Mean equivalent of these acids.}}$$

$$+ \frac{\text{oleic acid}}{282} + \frac{\text{linoleic acid}}{280} + \frac{\text{saturated acids in mixed part}}{x}$$

This gave the following results when applied to the experimental data:

					Mean equivalent of saturated acids linked with unsaturated acids.	Ratio of mols. saturated acids per 100 mols. unsaturated acids.
Butter-fat "A"		207.9	106 : 100
" " "B"		211.8	108 : 100

(ii) From the differential determinations of each individual acid recorded on p. 90, the molecular ratios of the saturated and unsaturated acids can be directly derived (the ratios for each acid have been inserted in the fifth column of the tables indicated); these give the following values:

					Ratio of mols. saturated acids per 100 mols. unsaturated acid.
Butter-fat "A"	104 : 100
" " "B"	104 : 100

The agreement between the respective estimates for each fat is satisfactorily close, and the mean ratios 105:100 for butter-fat "A" and 103.5:100 for butter-fat "B" have been employed in the calculations which follow. It is readily possible, knowing this ratio, to deduce the general composition of the fats on the successive hypotheses that either dioleo-glycerides or triolein are completely absent (absence of mono-oleo-glycerides is inconsistent with the observed figures); the resulting data are as follows:

Molecular percentages.			Weight percentages.		
Mono-"oleo"- glycerides. Per Cent.	Di-"oleo"- glycerides. Per Cent.	Tri- "olein." Per Cent.	Mono-"oleo"- glycerides. Per Cent.	Di-"oleo"- glycerides. Per Cent.	Tri- "olein." Per Cent.
<i>Butter-fat "A."</i>					
54	46	—	51	49	—
77	—	23	74	—	26
<i>Butter-fat "B."</i>					
53	47	—	50	50	—
76	—	24	73	—	27

Therefore, in each of the original butter-fats, there cannot be *less* than about 36 per cent. of mono-oleo-disaturated glycerides, nor can there be *more* than 18 per cent. of tri-olein (or 35 to 36 per cent. of di-oleo-monosaturated glyceride). The actual values lie somewhere between the limiting figures given; in the absence of any direct method for determining triolein, this is as far as the analytical data take us.

We venture to predict, however, that the actual values are not widely removed from those for a mixture of mono-oleo-disaturated and dioleo-monosaturated glycerides. Our belief that triolein is not likely to be present in any large proportion is based (i) on the argument that, since it is now tolerably evident that simple triglycerides of the saturated acids are either absent from, or present in only minute amounts in butter and most other solid fats, there is no reason to suppose that oleic acid will tend to form triolein in large proportions, and (ii) on the absence of any positive indication of its occurrence in any fat hitherto investigated which contains sufficient saturated acid to provide mixed glycerides with all the oleic acid present.

SUMMARY.—Methods have been developed for the determination of the proportions of each of the fatty acids contained in butter fat, and for a semi-quantitative determination of the manner in which the acids are combined to form the component glycerides of the natural fat. The investigation has been carried out in connection with three samples of New Zealand butter, all of which gave results of a similar order.

The composition of the mixed fatty acids has been obtained by:

(i) Removing as much of the lower fatty acids as possible by prolonged distillation in steam, the steam-volatile acids being recovered and fractionally distilled in the form of free acids;

(ii) Separating the fatty acids non-volatile in steam into two groups by means of the lead salt and alcohol method, followed by conversion of the acids from the soluble and insoluble lead salts into methyl esters, which were quantitatively fractionated at low pressure in the usual manner.

The approximate composition of the fatty acids was: Butyric, 3; caproic, 2; caprylic, 1; capric, 2; lauric, 4; myristic, 11; palmitic, 28; stearic, 9; oleic, 33–34; and linoleic, 4–5 per cent. The values for the volatile fatty acids accord with recent determinations by other workers; the values for myristic, palmitic and stearic acids differ from many previously recorded, whilst there is consistent evidence of the presence of a small percentage of acids less saturated than oleic.

The procedure for the study of the component glycerides consisted in oxidising the butter-fat under conditions in which all unsaturated components were transformed into acidic products, whilst glycerides containing only saturated fatty acids remained unaltered. The latter were recovered, their proportion noted, and the composition of the mixed fatty acids contained therein determined as above. From the resulting data the following general conclusions were drawn:

(i) The butter-fats examined contained about 30 per cent. of fully-saturated glycerides. The fatty acids therein were the same as those in the whole fat, and in proportions not widely different from those of the latter; but a tendency was noted for the occurrence of somewhat less of the volatile fatty acids in the fully-saturated part, coupled with a correspondingly slight concentration of the higher saturated fatty acids in this group of the glycerides. It is probable that all these glycerides are of the complex mixed type.

(ii) The remainder of the fat (about 70 per cent.) consisted of mixed glycerides of saturated and unsaturated acids, the molecular proportions of the acids being about 104 mols. of saturated to 100 mols. of unsaturated acid. The amount of mono-oleo-disaturated glycerides in the original fat is *at least* 36 per cent., and there cannot be *more* than 18 per cent. of triolein (or 36 per cent. of dioleo-mono-saturated glycerides); although no positive data are available, it is quite probable

that but little tri-olein is present, and that the approximate composition (in round numbers) of the butter-fats examined is:—

					Per Cent.
Mixed fully-saturated glycerides	ca. 30
Mixed mono-oleo-disaturated glycerides	ca. 36
Mixed di-oleo-monosaturated	ca. 34

It may be noted that all, except the unsaturated acids, are comparatively evenly distributed throughout the whole fat.

These results, of course, do not necessarily hold in detail for butters produced from widely varying sources. The investigation is being extended to butters made from the milk of cows feeding on a variety of diets, including (if possible) cases in which hard and soft oilcakes have been respectively employed in the diet.

We desire to express our most cordial thanks to Messrs. Lever Bros., Ltd., who have assisted us by obtaining supplies of the butters which we have studied, by carrying out some of the determinations of the technical "constants" of the fats, and, especially, by the provision of a Research Studentship in the Department of Industrial Chemistry of this University, which has enabled one of us to pursue the research.

THE UNIVERSITY,
LIVERPOOL.

DISCUSSION.

The PRESIDENT said that in this remarkable and valuable paper (not the first which the Society had had from Professor Hilditch) the authors had dealt in a fundamental manner with a fat which many had to examine daily. He had a suggestion to make on one small point: Professor Hilditch seemed to wonder whether the accuracy of some of his results was not due to coincidence. Would it not be possible to apply this method of fractionation to known mixtures of fatty acids, so as to substantiate the percentage accuracy of his separation?

Mr. E. R. BOLTON remarked that he was struck by the dramatic way in which the paper opened, by pointing out that the data available were in a chaotic condition. Professor Hilditch had gone forward, step by step, and had given us absolutely new information. One of the most striking points was the fact that the butyric acid, as determined by the Kirschner method, was rather in excess of that actually present; this was interesting, as it had always been understood that the Kirschner method afforded a good measure of the butyric acid. Mr. Bolton then referred to the problem of the detection of carcase fat in butter, and mentioned that the problem had become a very live one in India, where certain castes were not allowed to eat any butter containing carcase fat. Government chemists, therefore, had to face this problem, and had considerable difficulty in proving a butter to be free from this fat. If it were possible to bring the stearic acid of pure butter fat within narrower limits than the 0 to 22 per cent. recorded by Mr. Mitchell, to evolve a method for its accurate and rapid determination, and to state that pure butter should not contain more than a certain amount of that acid, it might afford a means of settling the problem of the Indian chemists.

Mr. C. A. MITCHELL said the method devised by Professor Hilditch and his co-worker marked a great advance on the original oxidation method of Hazura

and Grüssner, which gave results of qualitative rather than quantitative value. With regard to Mr. Bolton's suggestion of using the proportion of stearic acid as a means of differentiating between butter fat and animal body fat, this was the goal to which Hehner and he (the speaker) had worked for months, but the idea had had to be abandoned owing to the very wide variations in the stearic acid content of butter fat. Most of the early experiments on the crystallisation of butter fatty acids from a solvent saturated with pure stearic acid gave deposits ranging from a mere trace up to about 6 per cent., but subsequently several undoubtedly pure samples gave deposits of 12 to 22 per cent., and subsequently this had been repeatedly confirmed. It was also an interesting confirmation that the amount of stearic acid found by Holland and Buckley in American butter fat was over 20 per cent.

Dr. H. E. Cox remarked on the fact that the Kirschner value was shown to give an apparent butyric acid content about 20 per cent. too high, and asked for information as to exactly what acids were represented by the Reichert-Meissl, Polenske and Kirschner values, respectively. There was sometimes observed in genuine butter an unusually large spread between the Reichert-Meissl and the Kirschner values, amounting to as much as 25 per cent. or more of the Reichert-Meissl value, which was a larger variation than appeared in Prof. Hilditch's figures for the sum of the capric, caproic and caprylic acids, part of which, with the butyric acid, accounted for the Reichert-Meissl value.

Professor HILDITCH, replying, said that with regard to the President's question as to whether it were not possible to test the accuracy of the results: this had been done in the case of comparatively simple mixtures, and the results could be relied upon, but it had not been done with more complicated mixtures, such as the particularly difficult mixture which resulted when C_4 and C_{10} acids were present. It might be a very good idea to try this.

Mr. Bolton and Dr. Cox had both mentioned the Kirschner number. Professor Hilditch did not think he could add much on this point to what had been said in the reading of the paper. As far as his figures were concerned, the butyric acid figure was more likely to be on the high side than on the low side, and probably the Kirschner value included caproic acid. What he was really trying to get at was the constitution of natural fats, as far as this method would take him, and the examination of the composition of the glycerides contained in the fats; butter fats were one section of the work.

With regard to the percentage of stearic acid in butter fat, on the whole he agreed with Mr. Mitchell. He had found that there was considerable variation.

Referring to the length of time taken by this test, Professor Hilditch stated that at the present time he and his co-workers were trying to see if they could work out a modified test occupying not more than two days. They were also studying the method from the point of view of analytical application. Regarding Dr. Cox's question with reference to the Reichert-Meissl and Polenske values, he really hesitated to say, but it was quite possible that the "spread" which was mentioned existed, but he did not see that this could really be correlated with the results recorded in this paper.

Electrolytic Determination of Lead in Urine.

By T. COOKSEY, Ph.D., B.Sc., F.I.C., AND S. G. WALTON.

NUMEROUS methods, both chemical and electrolytic, have been proposed for the determination of the small amounts of lead occurring in pathological urine, but those who attempt it appreciate the difficulty of determining this substance when present in minute quantity only and mixed with the comparatively large number of other substances, organic and inorganic, which form the normal constituents of urine. Under the legislation of the present day, by which employees who are proved to be suffering from occupational diseases are granted compensation, the accuracy of the determination of lead in urine is of considerable importance in the diagnosis of cases of plumbism due to conditions of employment. A large quantity of literature is available to chemists, describing various methods for the determination of lead, and suggesting modifications of such methods, with a view to obtaining more reliable results. But in all, difficulties more or less considerable are encountered, due to the fact that the lead to be determined must be separated in some form from the large quantity of material present.

In attempting to minimise these difficulties, the following electrolytic method, based on the precipitation of the lead as metal, has been worked out. It possesses certain advantages:—(1) It can be applied to the urine without previous treatment; (2) A very small addition of chemical reagents is required, and these can be very easily freed from lead. The length of time taken to obtain the final result is not appreciably shortened, but the actual time occupied in manipulation is small.

In our hands very satisfactory results have been obtained, and we are now asking that the method may be published in *THE ANALYST*, in order that it may be subjected to wider criticism.

The following are the details of the method:—The acidity of the urine is ascertained, methyl red being used as indicator, and therefrom is determined the amount of acetic acid that it is necessary to add to 500 c.c. of the urine (contained in a suitably shaped beaker) so that the total acid present is approximately equivalent to 3 grms. of acetic acid.

The solution is now electrolysed, the strength of current used being 0.3–0.4 amp. The platinum electrodes, consisting of cone and wire spiral (see Baird and Tatlock's Catalogue, 1928, C.7070) were those used for this purpose. They should be so connected that the lead is deposited on the spiral, which should reach to within 1 cm. of the bottom of the beaker. It is advisable to select a narrow shaped beaker, of 500 c.c. capacity, and 11 cm. high, in order to promote an efficient circulation of the liquid.

When the electrolysis (which can proceed overnight) is finished—after 16 or 17 hours—a small amount of phosphate is sometimes found adhering to the cathode. The beaker containing the urine is carefully removed while the current is still passing, and immediately replaced by one of the same height but half the capacity, containing 250 c.c. of distilled water and 1 c.c. of strong hydrochloric acid. The passage of the current is allowed to continue for 2 hours. At the end of this time it will be found that all the phosphate has been dissolved. This beaker is now replaced (with the current still flowing) by one of the same size containing 250 c.c. of distilled water, which is allowed to remain for half-an-hour. It is then removed and the current switched off.

After that part of the cathode which remained above the level of the liquid has been wiped clean to remove adhering spray, the cathode is washed with alcohol and allowed to dry. The lead is dissolved in 4 c.c. of strong hot nitric acid by pouring the acid over the cathode several times. This solution is transferred to a small glass crystallising dish. The cathode is again treated in the same manner with a hot mixture of 1 c.c. of strong nitric acid and 9 c.c. of distilled water, and finally washed, 5 c.c. of hot water being used.

The whole is evaporated to dryness over the water bath, 1 c.c. strong hydrochloric acid added, and the solution again evaporated to complete dryness. The residue is warmed with 0.1 to 0.2 c.c. of hydrochloric acid and a few drops of distilled water, and 4 c.c. of distilled water added to the solution, which is again warmed on the water bath to ensure complete solution.

The liquid is transferred to a graduated measure and made up to 6 c.c., and 3 c.c. of this solution are transferred to one of a number of small test tubes which are marked at 3 c.c. A standard solution containing 0.00001 grm. of lead per c.c. is prepared and added to a series of comparison tubes (of the same bore and colour) in the following amounts:—0.0 c.c., 0.5 c.c., 1.0 c.c., 1.5 c.c., 2.0 c.c., 2.5 c.c., and 3.0 c.c. To each tube is then added the same amount of hydrochloric acid as that contained in the solution to be tested, and the volume made up to the 3 c.c. mark with distilled water. Two c.c. of a *freshly prepared* saturated solution of potassium metabisulphite are then added to each, and the contents of the tubes are well mixed, and the tubes corked and allowed to stand for 1–2 hours, after which the tube contents are again well mixed, and the turbidity of the sample tubes compared with that of the standards.

If the lead content is heavy, a smaller quantity than 3 c.c. should be taken for the determination, and made up to 3 c.c. with distilled water and sufficient hydrochloric acid to preserve the same acidity as in the standards.

As it may occasionally happen that a small proportion (usually, however, not more than one-tenth) of the lead present is not removed in the first electrolysis, it is advisable to submit the sample and washings to a second treatment. After electrolysis the urine contained in the beaker is heated on the water bath for one hour, cooled, and made up to the original volume with distilled water. In the event of a deposit of phosphate forming in the cathode during the first electrolysis,

0.5 c.c. of glacial acetic acid is added, and the urine again electrolysed overnight. The hydrochloric acid and the water washings from the first electrolysis are combined and heated on the water bath for one hour, cooled, 1 c.c. of strong hydrochloric acid added, and the volume made up to 500 c.c. This solution is used for the first washing of the electrode in the second electrolysis, the current being passed for 2 hours. The wash is immediately replaced by one containing 250 c.c. of distilled water. The cathode is again treated in the same way as in the first electrolysis. Any lead present is added to that found previously.

It is of advantage to have a considerable reserve of voltage, which is made use of during the washing stages. For the purposes of checking materials, a blank experiment should be carried out with the glassware, electrodes and reagents made use of in the analysis.

Normal urine examined by this method was found to possess a lead content varying from 0.02 to 0.05 mgrm. per litre, averaging 0.04 mgrm. per litre. The method, as described, is intended for the determination of the very small amounts of lead occurring in urine, and the accuracy of its results compares very favourably with those obtained by other methods in use. Any small error made in the comparison of the lead sulphite precipitates will necessarily be multiplied in the determination of amounts considerably larger than those usually occurring, but in such cases the method of determination of the amount of lead deposited on the cathode may be varied as found necessary.

OFFICE OF THE DIRECTOR GENERAL OF
PUBLIC HEALTH, SYDNEY, N.S.W.

The Solubility of Reinsch Antimony Films in Water.

By S. G. CLARKE, B.Sc., A.I.C.

IN almost all of the papers on the quantitative application of the Reinsch test for antimony (deposition on copper from a halide solution) special mention has been made of the necessity, in stripping the deposited film, of allowing as little time as possible to elapse between removing the antimony-coated coil from the boiling solution at the end of the deposition and immersing it in the stripping solution. The reason given for this is that the coating is liable to undergo a change which renders it partly insoluble in the stripping reagent. My experience is that this is more likely to happen with films containing more than 0.0010 grm. of antimony than with smaller amounts; which is perhaps the reason why I have rarely encountered this troublesome feature in dealing with a very large number of determinations of minute amounts of antimony.

There is another, and perhaps more important, reason why no delay should take place between removing the coil after deposition and stripping it. It is, of course, necessary to wash or rinse the coil with water as an intermediate step between the above two operations. The purpose of this note is to direct attention to the fact that if this washing is unduly prolonged, or, indeed, not carried out as rapidly as possible, distinct amounts of antimony are removed from the coil when ordinary distilled water is used. Series of experiments which have been carried out on the following lines show that this solubility of the deposited antimony film is due to the presence of dissolved oxygen in the distilled water.

A number of strips of pure electrolytic copper foil, 20 cm. \times 2.4 cm., were coiled into flat, rather open, spirals, cleaned by immersion in dilute nitric acid (sp. gr. 1.2) and well washed; 0.0005 grm. of antimony was then deposited on each by the Reinsch reaction. Each coil was withdrawn from the boiling solution by means of a hooked glass rod, washed free from acid by dipping into a large volume of distilled water (the time taken in this washing was, on the average, approximately two seconds), and then at once immersed for a definite time in 50 c.c. of ordinary distilled water contained in a 100 c.c. beaker. The water was poured off promptly at the end of the time, and the antimony which had passed into solution was determined as follows:

Five c.c. of 20 per cent. sodium hydroxide solution were added, and hydrogen sulphide passed through the liquid for 15 seconds; a trace of copper accompanying the antimony was thereby precipitated and was allowed to settle out on a water bath and finally filtered off. Five c.c. of concentrated sulphuric acid were added to the filtrate, which was then evaporated until it just fumed; after cooling, this was taken up in 15 c.c. of water, heated to boiling and cooled, and the antimony determined colorimetrically by the pyridine and iodide method described fully in an earlier paper (Clarke, *ANALYST*, 1928, 53, 373).

Results were obtained as follows:

	Antimony on copper. Grm.	Time of immersion.* Minutes.	Standard antimony solution required.† c.c.	Antimony dissolved. Grm.
(1)	0.0005	1	0.15	0.000015
(2)	0.0005	2	0.3	0.00003
(3)	0.0005	5	1.2	0.00012
(4)	0.0005	10	1.5	0.00015
(5)	0.0005	15	1.7	0.00017
(6)	0.0005	25	1.9	0.00019

* The water was not stirred during the immersion. It was neutral in its reaction to litmus.

† Standard antimony solution = 0.0001 grm. per c.c.

With the exception of (3), the above figures, when presented graphically, produce a smooth curve which becomes almost parallel with the time axis as the time of immersion increases, indicating removal, to a great extent, of the factor causing solution as more antimony enters solution. This lends support to the view that the solution of the antimony is due to dissolved oxygen. The following

experiments afford confirmation of this. In these tests distilled water, which had been boiled and cooled rapidly immediately before use, was used for the immersion of the coils. The coils were rinsed, as before, with ordinary distilled water.

Antimony on copper. Grm.	Time of immersion. Minutes.	Antimony dissolved. Grm.
0.0005	1	nil
0.0005	2	nil
0.0005	5	nil
0.0005	15	0.000015

The trace of antimony dissolved in the last test is doubtless due to absorption of oxygen during the immersion.

The main fact which emerges is that it is not necessary to use boiled-out water for washing Reinsch coils after deposition; ordinary distilled water may be used, provided that washing does not occupy more than a few seconds.

RESEARCH DEPARTMENT,
WOOLWICH.

Notes.

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

MEASUREMENT OF THE STRENGTH OF SUNLIGHT.

THE following description of a method which has been in use at Salford for the past three years, for the purpose of comparing the relative *strength* of sunlight in various districts (as distinct from the actual *amounts*), may be of interest to those interested in the smoke-pollution problem. It is well known that the blanket of smoke which hangs over most large towns is instrumental in robbing the sunlight of a large part of its hygienic value, to the detriment of the health of the inhabitants of the district. The ultra-violet rays are the first to be cut off by the smoke-polluted atmosphere, and the absence of these is partly responsible for the development of rickets, anaemia, and tuberculosis, particularly in children.

It is claimed that by the method given here the comparative chemical activity of the light received at different stations can be measured with reasonable accuracy, provided that the tests are carried out at each of the places under conditions as similar as possible.

The method, which was described by the Manchester Air Analysis Committee in 1924, consists in exposing in glass bottles a solution of potassium iodide acidified with sulphuric acid, in the presence of air, to the action of the light. Free iodine is liberated, and the amount is proportional to the chemical activity of the light received. The percentage of ultra-violet light transmitted by ordinary glass is very small, but sufficient for the purpose of giving comparative results.

The strengths of the solutions found to be most convenient are as follows:—Potassium iodide, 20 grms. per litre; sulphuric acid, *N*/4 approx.; sodium thiosulphate, 1 c.c. equals 0·001 grm. of iodine.

Two-ounce stoppered bottles are used for the actual tests. Ten c.c. of potassium iodide solution and 10 c.c. of the sulphuric acid are pipetted into a bottle, which is then placed on a 6-inch white tile in an open position where no shadow will fall on it during the day. It is left exposed for 24 hours, and its contents then titrated with the thiosulphate solution. If any delay is likely to occur between the removal of the bottle and its titration, the bottle may be kept in a small closed tin until ready, so as to prevent any further action of the light.

The result of the titration is recorded as mgrms. of iodine. A fresh bottle should be exposed at the end of every 24 hours. The change should, of course, be made at the same time each day, particularly in the summer.

Any blank on the iodide solution is allowed for by making up a second bottle at the same time as the one to be exposed and keeping the former in a closed tin until the exposed solution is titrated.

The seasonal variations in the activity of the sun's rays are illustrated by the following monthly tables for the Regent Road station for 1927. This station is in a congested quarter of Salford:

		Mgrms.			Mgrms.
January	..	41·2	July	..	208·0
February	..	68·5	August	..	178·6
March	..	159·6	September	..	118·7
April	..	148·7	October	..	65·5
May	..	188·6	November	..	68·5
June	..	179·4	December	..	42·0

The totals for the two half years of 1926 and 1927 for all the four stations at which tests have been carried out are as follows:

1926.

	Regent Road. Mgrms.	Nab Top Sanatorium Marple. Mgrms.	Ladywell Sanatorium. Mgrms.	Drinkwater Park. Mgrms.
First half year	.. 744·5	885·8	842·9	876·9
Second „ „	.. 869·2	860·8	812·0	870·3

1927.

First half year	.. 786·0	911·8	952·5	1036·2
Second „ „	.. 681·2	766·7	792·9	809·9

It will be remembered that 1926 was marked, during the latter half of the year, by the coal stoppage. This affected the amounts of dust and smoke in the atmosphere to a considerable degree, and the figures given above for 1926 reflect the unusual conditions then prevailing.

The station at Nab Top is several miles from Salford, in Cheshire; Ladywell Sanatorium is on the outskirts of the City, and Drinkwater Park is outside the City boundary in the neighbouring district of Prestwich. None of these three stations is affected to anything like the same degree as the Regent Road station by the effects of the combustion of coal, and the atmosphere, in comparison to that of the latter, is relatively free from smoke. It will be seen that the total for Regent Road for the first half year is considerably lower than those for the

other three stations, but that during the second half year, whereas the totals for the outlying stations were approximately the same as for the first half year, the total for Regent Road was some 17 per cent. higher, and when it is remembered that the atmosphere during these six months was marked by a cleanliness hitherto unknown, due to the enforced restricted use of raw coal, the connection between the fact and the increased activity of the sunlight, will be appreciated.

The figures for 1927 show no such striking results, and the Regent Road station, for both the half yearly periods, received less active sunlight than the other three.

Another significant fact with regard to the monthly figures is that during the summer months the figures for Regent Road more nearly approached those for the outer stations, and on two or three occasions actually exceeded the figures for one or two of the latter. This is probably due to the fact that less coal is burnt in the summer months, and also to the absence of part of the population on holiday.

The method described is obviously of value in emphasising the need for some form of smokeless fuel for use in the domestic grate, which has been proved to be the chief offender in rendering the atmosphere so unfit to breathe.

H. H. BAGNALL.

MUNICIPAL LABORATORY,
SALFORD.

Notes from the Reports of Public Analysts.

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF LEEDS.

REPORT OF THE CITY ANALYST FOR THE THIRD QUARTER, 1928.

ANALYTICAL work was commenced in the newly-equipped laboratories at No. 1, Swinegate, in the early part of July.

Of the 377 samples examined, 332 (326 formal and 6 informal) were taken under the Sale of Food and Drugs Acts, 1875-1927, 8 (4 formal and 4 informal) under the Fertilisers and Feeding Stuffs Act, 1926, and 5 (formal) under the Rag Flock Acts, 1911 and 1928. Of the food and drugs samples, 59 (57 formal and 2 informal), or 17·8 per cent., were adulterated.

MILK.—Fifty-one of 237 samples (234 formal and 3 informal) examined were below standard.

It has transpired that some farmers producing Grade A milk make a practice of bottling the milk from individual cows instead of the mixed product of the whole herd. This may explain in part the low fat content of some of these milks, though it is not suggested that fat deficiencies of 18 to 20 per cent. are thus wholly accounted for.

POTTED MEAT.—Of 13 samples examined, 3 contained 6·0, 7·5 and 0·8 per cent. starch, respectively; the remaining samples were free from starch. In the first case the manufacturer is now selling the article under a different name.

SWEET NITRE.—Of 4 samples examined, 3 were deficient in ethyl nitrite to the extent of 9.9, 31.0 and 100.0 per cent. respectively, calculated on the minimum of 1.52 per cent. of the active principle. Proceedings were instituted in the second and third cases, the retailers concerned being ordered to pay costs. In the 100 per cent. deficiency case the article sold proved to consist of an aqueous alcoholic solution of 3.7 per cent. ammonium acetate and 15 per cent. of sucrose; it has been supplied to the retailer as "Nitric Sweating Mixture."

TOXICOLOGICAL ANALYSIS.—The organs of an elderly man, suspected of having died from sheep-dip poisoning, were submitted for analysis. This case, following closely upon the Pace trial, excited considerable interest. No poison was found, and the sheep-dip, moreover, proved to be a non-arsenical preparation possessing a creosote acid basis.

C. H. MANLEY.

GIBRALTAR.

ANNUAL REPORT OF THE CITY ANALYST AND BACTERIOLOGIST FOR 1927.

THE number of samples of foods and drugs examined under the Public Health Ordinance during the year was 168, of which 24 were below the official standards.

GOATS' MILK.—Of the 56 samples examined, 10 were deficient in fat, 4 contained added water, 1 showed both abstraction of fat and added water, and 4 contained unboiled milk. The statutory limits for goats' milk are 3.5 per cent. of fat and 8.0 per cent. of solids-not-fat. As pointed out in previous reports, some milk vendors habitually remove the scum which rises to the surface on boiling, to improve the appearance, thereby robbing the milk of a proportion of its fat. In view of the fact that vendors of boiled goats' milk declare the milk "skimmed," thus evading the law, amendments to the Public Health Ordinance are under consideration, and include the following:—"No sample of boiled *scummed* goats' milk shall contain less than 3.5 per cent. of milk fat." It is expected that this will become operative in the near future.

Goats' Unboiled Milk.—While no sample of raw imported milk was discovered there were, however, four samples showing some contamination with unboiled milk. By law no imported milk may be offered for sale to the public unless it has been boiled in Gibraltar. This is a necessary precaution against milk-borne diseases, the Council having no control over the source of production.

CONDENSED AND DRIED MILK.—An Ordinance has been prepared, based on the standards required in England, and is expected to come in force within the year.

BACTERIOLOGY AND HEALTH WORK.—During the year the number of samples and specimens examined was 4188, including drinking waters, swabs, blood, faeces, and human milk. The serological agglutination test was carried out on the 209 goats living on "The Rock." All were found free from undulant fever. One hundred and twenty-one rats, caught on the quays or in Gibraltar, were examined for the plague bacillus; all were free.

A. G. HOLBOROW.

Legal Notes.

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

"EGG FLOUR."

ON November 28, a grocer was summoned at Lichfield for selling "egg flour" containing no eggs.

According to the prosecution an inspector purchased a packet of egg flour at the defendant's shop for 5½d. The packet was advertised as "——'s, Beat All Egg Flour. Requires no eggs, egg powder, or baking powder." The cost of the best self-raising flour should not exceed 3d. per packet.

The County Analyst (Mr. E. V. Jones), giving evidence, said that the flour was devoid of egg, and consisted of self-raising flour to which had been added a small percentage of coloured maize, prepared in such a manner as to resemble flour containing small lumps of dried egg, which was very misleading to the public and most unfair to manufacturers of the genuine article.

The defendant said that he did not buy the colour, but that he had bought the maize as an egg substitute. The article was originally known as "Tingle's Egg Flour"; it had been made in Lichfield for 30 years, and he himself had been making it for 12 years. He had omitted to change the name to "egg substitute."

A fine of 10s., with £6 15s. 6d. costs, was imposed.

"HOME-MADE" LEMON CHEESE.

ON December 5th a shopkeeper was summoned before the Stipendiary Magistrate of Salford (Mr. P. W. Atkin), for selling home-made lemon cheese not of the nature, substance and quality demanded, and the makers were also summoned under Sec. 27 of the Sale of Food and Drugs Act, 1875, for giving a label falsely describing the article.

Mr. H. H. Tomson, Deputy Town Clerk, prosecuting on behalf of the Health Committee, said that the Food and Drugs Inspector, by means of his deputy, purchased two small jars of home-made lemon cheese at the defendant's shop for which he paid 1s. 1d.

The sample was analysed by the City Analyst (Mr. H. H. Bagnall), and his certificate stated that "Home-made lemon cheese should consist of butter, sugar, eggs and lemon juice and rind. The fat in this sample consists of margarine, cane sugar is replaced to the extent of 39 per cent. by glucose syrup, and the protein content indicates the presence of not more than the merest trace of eggs. It contains about 8 per cent. of water in excess of that associated with fat, protein, glucose, starch, and lemon products, and is artificially coloured. This is not home-made lemon cheese, as two of the principal constituents, butter and eggs, are practically entirely absent, and sugar is replaced to a large extent by glucose syrup. The starch is a foreign ingredient and should not be present at all." Mr. Tomson said that it was not submitted that the article was unwholesome, but it was not home-made. There were many articles on the market equal to this at half the price.

In pleading guilty, one of the partners of the firm stated that they sold the article as they received it. In the case against the makers, Mr. Tomson contended that the glass jars were made up in a way that was calculated to deceive the ordinary housewife. The lithographed label bore the words "Home made" in imitation script.

"There is no statutory standard for lemon cheese," Mr. Tomson proceeded, "but my submission is that an article which is described as home-made should be made of materials which one would expect to be used in an ordinary domestic household. This is not a home-made lemon cheese because it is made in a factory and sold wholesale throughout the country. I am not, however, challenging the wholesomeness of the commodity."

Evidence was given by the Public Analyst (Mr. H. H. Bagnall), by the Lancashire County Analyst (Mr. G. D. Elsdon) and by the Food Inspector, to the effect that, while there was no legal standard for lemon cheese, custom fixed the standard that it should be made from butter, sugar, eggs and lemons. There was no objection to the article in question if it was not sold as home-made.

Mr. V. Parker, for the defence, suggested that a purchaser would not be deceived by the label, and said that if it had been intended to imply that the article was made on the shopkeeper's premises, the words "Our own make" would have been used. The label did not necessarily mean that the commodity was made on the premises at which it was sold. The firm was giving people value for their money, and the purchaser was getting a perfectly pure and wholesome article.

On the summons against the shopkeeper a fine of £5 was imposed, and the makers were fined £5, with £15 special costs, the Stipendiary remarking that a home-made article should, in his opinion, be made from ingredients that the ordinary housewife would use.

BORIC ACID SOLD AS A FOOD PRESERVATIVE.

ON December 6, a druggist was summoned at Barnsley, under the Public Health (Preservatives, etc., in Food) Regulations for selling boric acid with a recommendation that it was a food preservative.

Mr. N. P. Lester (Assistant Town Clerk) explained that only two articles could be sold as food preservatives, and that in this case boric acid (which was not one of the approved articles) had been sold in a container which recommended it as a preservative of milk.

Mr. N. Goodyear, for the defence, pleaded guilty to a technical offence, but contended that, although there was nothing to prevent anyone buying boric acid and using it as a food preservative, yet an offence was committed when the seller recommended its use for that purpose. The Regulations under which the proceedings were taken had only come into force at the beginning of the year, and it was difficult for druggists' assistants to keep pace with the numerous regulations that were being made.

The Magistrates decided that the offence was due to a misunderstanding, and dismissed the summons on payment of costs.

Department of Scientific and Industrial Research.

REPORT OF THE WATER POLLUTION RESEARCH BOARD FOR THE YEAR 1927-28.*

THE objects of the Water Pollution Board are to collect and collate all pertinent scientific and technical information, so that it may be readily available for practical application by those who are concerned with water supply and the disposal of polluting liquids; to encourage and co-ordinate relevant scientific research in this country; and to undertake such investigations as are necessary in the public interest and not otherwise provided for. A survey of the River Tees is in view in conjunction with the Tees Fishery Board.

In considering water-supply it is proposed particularly to investigate the base exchange or zeolite treatment of water, with special reference to the rate and extent of the base exchange; wastage of material; possibility of contamination of the softened water by silica and alumina; how far the action is a surface one, depending upon size and texture of particles; and the process of regeneration. With regard to sewage disposal, the activated sludge process is to be investigated on biological lines, and in the case of the treatment of industrial effluents a beginning has been made with beet sugar factories effluent, and the experiments, though not yet complete, suggest that a practical solution will be found in biological filtration.

The ideal solution of the problem would be such an alteration of processes that no waste water would be discharged, and, as a rule, less drastic treatment should be needed to render the waste waters fit for re-use than for discharge. The removal of suspended solids by means of detritus tanks, reasonably small; a graded series of mechanically operated and cleaned screens, and finally sedimentation tanks are suggested. Fine screening is not advocated, and punched metal screens would obviate the difficulty of leaves, beet debris, etc., getting entangled in the mesh of woven screens. The sugar and dissolved organic material not removed in such a plant, by gradual accumulation would be liable to fermentation, so that a proportion of treated water would need to be discharged daily and the loss made up with fresh water.

D. G. H.

* Obtainable at H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 6d. net.

U.S.A. Department of Agriculture.

STANDARD FOR MAYONNAISE SALAD DRESSING.

ACTING upon the recommendation of a joint Committee, including representatives of the Association of Dairy, Food and Drug Officials of the United States, the Association of Official Agricultural Chemists, and of the United States Department of Agriculture, the Secretary of Agriculture has adopted the following definition and standard for mayonnaise salad dressing.

MAYONNAISE, MAYONNAISE DRESSING, MAYONNAISE SALAD DRESSING is the clean, sound, semi-solid emulsion of edible vegetable oil and egg yolk or whole egg, with vinegar or lemon juice, and with one or more of the following: Salt, spice, sugar. The finished product contains not less than 50 per cent. of edible vegetable oil, and the sum of the percentages of oil and egg yolk is not less than 78.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Determination of Honey in Honey Cake. R. T. A. Mees. (*Chem. Weekblad*, 1928, **25**, 674–676.)—It is shown that since the composition of the sugars used in the manufacture of honey cake is almost unaffected by the baking process, the percentage of fructose in an extract of the cake may be taken as a measure of the amount of honey used. The fructose is determined on an extract prepared by grinding 30 grms. of cake with water in a mortar, the volume being made up to 200 c.c. and the mixture centrifuged and filtered. The same solution may be used for the determination of the extract from the specific gravity. To 2.5 c.c. of a *N* solution of iodine and 3 c.c. of *N* sodium hydroxide solution are added 20 c.c. of the ten-fold diluted extract. After 5 minutes in the dark the solution is acidified with 1 c.c. of 4 *N* hydrochloric acid and then titrated with a 10 per cent. solution of sodium sulphite, the exact end-point being finally obtained by means of a 5 per cent. solution as in the method of Kolthoff (*ANALYST*, 1922, **47**, 301; 1923, **48**, 386). If 20 c.c. of mixed Fehling's solution are then added to the mixture (about 30 c.c.) the reducing powers of the solution may be determined, and the result calculated as percentage of fructose. The method has been tested on pure sugars and on sugar mixtures and cakes of known composition, and gives results which are higher and nearer the true values than those obtained by Kolthoff's method or by the usual indirect polarimetric method. Of 77 commercial samples of cake, about half were considered to contain natural honey, and the fructose content varied from 4 to 37 per cent.

J. G.

Quantitative Determination of Oxymethylfurfural in Honey. J. Fiehe. (*Z. Unters. Lebensm.*, 1928, **56**, 200–203.)—In Troje's method (*Z. Ver. deut. Zuckerind.*, 1925, **75**, 635) an extract of the honey in anhydrous ethyl acetate is evaporated *in vacuo* at 45° C., and the residue oxidised by an alkaline solution of iodine, the excess of which is back-titrated with sodium thiosulphate solution. It is shown that the method is affected by the presence of sugars, organic acids, aromatic compounds, colouring matters and other substances in the honey, and may therefore give high values indicating an oxymethylfurfural content, even when this substance is absent.

J. G.

Occurrence, Detection and Determination of Lauric Acid in Alcoholic Beverages. J. Grossfeld and A. Miermeister. (*Z. Unters. Lebensm.*, 1928, **56**, 167–187.)—Lauric acid (0.2 mgrm.) may be detected in the presence of myristic acid or 3 mgrms. of caproic acid by the extraction of 50 c.c. of the sample with 50 c.c. of ether, the residue after evaporation of the ether being dissolved in 3 c.c. of alcohol, and boiled under a reflux condenser for 10 minutes with

0.5 c.c. of 0.5 *N* alcoholic potassium hydroxide solution. The residue left on evaporating the solution is then dissolved in 3 c.c. of water and heated on the water-bath for 5 minutes with 0.2 c.c. of glycerin. The addition of 0.25 c.c. of 15 per cent. magnesium sulphate solution, followed by filtration while hot through a tightly packed asbestos filter, gradually produces a precipitate of magnesium laurate. For the determination of the lauric acid, 500 c.c. of the sample and 300 c.c. of water are distilled, and the distillate (450 c.c.), together with the 50 c.c. of alcohol used to wash the condenser, is boiled under a reflux condenser for 30 minutes with 5 c.c. of a 75 per cent. solution of potassium hydroxide. The solution is evaporated, and the residue is dissolved in 25 c.c. of a solution of 25 grms. of sodium acetate, 5 c.c. of glacial acetic acid and 1 c.c. of 1 per cent. phenolphthalein solution in 250 c.c. of water, and 30 per cent. acetic acid is added till only a faint red colour remains, which is then removed by one drop of the acetate solution and restored by addition of 0.1 *N* sodium hydroxide solution. After filtration in the presence of kieselguhr the solution is boiled, 5 c.c. of the magnesium sulphate solution added, and any red colour again dispersed by the acetate solution. After 24 hours the precipitate is filtered on a Gooch crucible previously washed with a little magnesium laurate solution and dried in the steam-oven, dried, washed, gently heated and the crucible re-weighed. From the loss in weight, which gives the lauric anhydride, the factor 1.105 is used to obtain the magnesium laurate, and after a correction for the solubility of that salt (0.5 or 0.6 mgrm., according to whether the volume is 40 to 43 c.c. or 44 to 50 c.c., respectively), the factor 0.9472 gives lauric acid. The caprylic acid value is determined by the addition of 1 c.c. of a 50 per cent. solution of potassium hydroxide to the distillate (95 c.c.) obtained from 100 c.c. of sample. The mixture is boiled under a reflux condenser for 30 minutes, evaporated to dryness, the residue dissolved in 10 c.c. of water, neutralised to phenolphthalein with 30 per cent. acetic acid, diluted with 50 c.c. of water, and 25 c.c. of a 1.5 per cent. solution of magnesium sulphate added. After 24 hours the solution is filtered, 10 c.c. of a solution of 50 grms. of sodium acetate, 3.12 grms. of copper sulphate and 5 c.c. of 20 per cent. acetic acid per litre added, and the precipitate filtered off, dried and weighed on a Gooch crucible. The solubility correction is 0.7 mgrm., calculated as copper laurate, and the factor 0.869 then gives the caprylic acid value in c.c. of 0.01 *N* acid, whilst the factor 1.44 gives its weight in mgrms. It is concluded that the principal constituent of the so-called grape or cognac oils is lauric, and not capric acid, in the form of esters. The lauric acid content of a beverage does not appear to depend on the alcohol content. The acid can be removed from fusel oils by rectification, and is obtained in the "second runnings" during distillation.

J. G.

Sesamin and Sesamolin. W. Adriani. (*Z. Unters. Lebensm.*, 1928, 56, 187-194.)—The author distinguishes the following constituents of sesame oil, and complains of their confusion in the literature (*cf.* Hönig, *Chem. Weekblad*, 1925, 22, 509; Malagnini and Armanni, *ANALYST*, 1907, 32, 391):—*Sesamin*,

$C_{20}H_{18}O_6(?)$, may occur to the extent of 1 per cent., and has been isolated by crystallisation from alcohol as long colourless needles, m.pt. $122.5^\circ C.$, $[\alpha]_D^{20} + 68.23^\circ$ (chloroform), sparingly soluble in ether or petroleum spirit and easily soluble in acetone or chloroform. It differs from phytosterol in that it gives Bömer's reactions (a green colour turning to red and then to reddish-blue when shaken with equal parts of concentrated sulphuric acid and acetic anhydride, and a cherry-red colour turning to blue when a solution in chloroform is shaken with one drop of concentrated sulphuric acid), but it does not give Baudouin's reaction. *Sesamol*, $C_7H_6O_3$, m.pt. $65.5^\circ C.$, occurs to the extent of 0.1 per cent., has a phenolic odour and gives the Baudouin and Kreis tests (a pine chip dipped in the sesamol and then in concentrated hydrochloric acid gives a green colour). *Sesamolin*, m.pt. $93.6^\circ C.$, $[\alpha]_D^{20} + 218.4^\circ$ (chloroform), also gives Baudouin's test, since hydrochloric acid converts it into sesamol and samin, $C_{20}H_{18}O_7 + H_2O = C_7H_6O_3 + C_{13}H_{14}O_5$. It constitutes 0.3 per cent. of the oil. *Samin*, $C_{13}H_{14}O_5$, was isolated as long colourless needles, m.pt. $103^\circ C.$, $[\alpha]_D^{20} + 103^\circ$ (chloroform). J. G.

Luminescence of Oils and Fats. A. van Raalte. (*Z. Unters. Lebensm.*, 1928, **56**, 195-198.)—The author provides further evidence in favour of his hypothesis that the appearance of luminescence in refined oils and fats is due to the removal of vitamins which inhibit luminescence in the crude product. For example, vitamins may be produced in certain fats by exposure to sunlight, and their powers of luminescence then disappear (see, however, Carrière, *Chem. Weekblad*, 1928, **25**, 632). The conclusions of Feder and Rath (*Z. Unters. Lebensm.*, 1927, **54**, 321) are also criticised. (Cf. *ANALYST*, 1928, **53**, 617.) J. G.

Volumetric Method for the Determination of Tin in Preserves and other Foodstuffs. B. Glassmann and S. Barsutzkaja. (*Z. Unters. Lebensm.*, 1928, **36**, 208-212.)—The mixed sample (50 grms.) is dried, ignited, the ash extracted with 30 c.c. of dilute nitric acid (1 : 2) to remove iron, copper and lead, and after filtration the residue and paper again ignited. The tin is then reduced to metal by fusion at low red-heat with 1 gm. of potassium cyanide, the melt extracted with 150 c.c. of water, and the residue (and filter), after filtration of the extract, digested with 25 c.c. of concentrated hydrochloric acid in a flask fitted with a Bunsen valve. One gm. of zinc is added to complete the reduction, the solution cooled in a stream of carbon dioxide, and titrated with a 0.02 *N* solution of potassium dichromate in the presence of a little potassium iodide with starch indicator. The dichromate solution is standardised against a solution containing a known amount of pure tin prepared in a similar way. The method, which takes about 6 hours, has been applied to fish products, a maximum error of -7 mgrms. being recorded for a tin content of 50 mgrms. (-2.5 mgrms. for 10 mgrms. tin). The tin content of a $2\frac{1}{2}$ years old sample, kept in the open tin container for 12 days, rose from 154.6 to 420 mgrms. per kilo. J. G.

Determination of Caffeine in Tea. S. Gobert. (*Ann. Falsif.*, 1928, **21**, 517-518.)—Three grms. of the very finely powdered sample of tea are moistened

with 4 c.c. of ammonia, which causes the cells to swell and admit solvent, and also sets free combined caffeine. After half an hour four ethyl acetate extractions are made, each with 25 c.c., and the dried extract is purified by mixing with 4 c.c. of ammonia (22° Bé), and, after standing, is extracted 4 times with 25 c.c. portions of ethyl acetate. After centrifuging for 5–7 minutes and decanting, the ethyl acetate is distilled off, and the residue dried. It is then twice extracted with 50 c.c. and once with 25 c.c. of boiling water, 15 c.c. of 1 per cent. potassium permanganate solution are added to the extract, and after 15 minutes the manganese is precipitated by 12 volume hydrogen peroxide containing 1 per cent. of glacial acetic acid. The filtrate is then evaporated, and the residue dried, extracted 3 times with chloroform, and weighed. A moisture determination is made at the same time. Very closely agreeing duplicate results were obtained on samples of Ceylon tea.

D. G. H.

Determination of Morphine. A. K. Balls and W. A. Wolff. (*J. Biol. Chem.*, 1928, 80, 379–402.)—The determination of morphine in biological material is difficult and tedious. The existing methods have been subjected to a critical study, and their sources of error are pointed out. All the methods consist of two parts: first, isolation of the alkaloid in a state of relative purity; second, measurement of its amount. When morphine is isolated by the precipitation of accompanying impurities, there is apt to be a retention of morphine by the precipitate, which cannot always be removed by exhaustive washing. Methods which avoid precipitation frequently require evaporation of neutral or alkaline morphine solutions, and this decomposes a considerable amount of morphine. The decomposition products may follow the morphine through the analysis, and may finally be determined with it, because of the similarity in their reactions, but this precludes any distinction between morphine and its oxidation products in the original material. Control determinations on tissues which contain known amounts of morphine may give satisfactory results, but may not indicate that the method is suitable for the determination of unchanged morphine in the presence of oxidised morphine. A series of methods for the determination of morphine in biological material is proposed which, it is hoped, eliminates many of these errors. The methods are unsuitable for amounts of morphine less than 20 mgrms. per 100 grms. of material, but, where applicable, they possess the advantages of rapidity, simplicity, exclusion of the oxidation products of morphine, and inclusion of a desirable check on the final result. Methods are described for morphine determination in muscle, urine and blood. Provided the isolation process has yielded pure morphine, almost any of the methods of final determination are satisfactory, and the authors have selected from among the gravimetric determinations the silicotungstic acid precipitation of Bertrand (*Compt. rend.*, 1899, 128, 743), given in detail for morphine determination by Balls (*J. Biol. Chem.*, 1926–27, 71, 543), and chosen on account of the valuable check which may be made on the validity of the results.

P. H. P.

Action of Schiff's Reagent on Pyramidone. A. Valdiguié. (*J. Pharm. Chim.*, 1928, 120, 506-510.)—The addition of a few drops of Schiff's reagent (made up according to any of the formulae, provided an excess of sulphur dioxide is avoided) to an alcoholic or water solution of pyramidone or its salts, such as the camphorate or salicylate, provided the solution is not too acid, produces a red coloration. In the absence of other substances giving a reaction with Schiff's reagent, the reagent may be used for a colorimetric determination, and the limit of sensibility is about 1 part in 10,000. The colour is not affected by air or light, and is more red than violet. A critical study of the reaction suggests that a molecular combination of the sulphited rosaniline and pyramidone takes place.

D. G. H.

Biochemical.

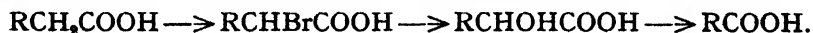
Distribution of Unsaturated Fatty Acids in Tissues. III. Vital Organs of Beef. W. R. Bloor. (*J. Biol. Chem.*, 1928, 80, 443-454.)—Data have previously been presented by Bloor on the unsaturated fatty acids of the heart (*J. Biol. Chem.*, 1926, 68, 33) and other muscles (*J. Biol. Chem.*, 1927, 72, 327) of the ox, and similar data are now given as to the more important vital organs of the same animal. A table of results shows that the lipid content of the organs varied greatly both for the same organ and for different organs. The constituent which varied least for each organ (not more than 30 per cent. above or below the average value) was the total phospholipid, which was relatively constant, and may therefore be regarded as a tissue constant characteristic of the particular organ. The arrangement of the organs in the order of their phospholipid content gave a series which represented the order of their functional activity, namely, brain (highest), liver, pancreas, kidney, and lung. The similarity in the weights of lecithin and cephalin in the various samples of all tissues points either to an equimolecular equilibrium, or to an equimolecular combination, between the two. The average iodine values of lecithin and cephalin strongly indicated a close similarity between the two compounds. Certain organs showed higher iodine values for phospholipid than others, but the difference was not great, and this similarity points to a considerable basic content of the same phospholipids in all organs and tissues. The content of fatty acids found indicated that the lecithin fraction was quite pure, but that the cephalin and fat fractions contained considerable admixtures of other substances. The mixture of fatty acids obtained by saponification of the various fractions consisted, as in the muscles, of about one-half liquid or unsaturated acids and about one-quarter solid acids, the remaining quarter being unaccounted for, and thus constituting a problem which must be solved. The unsaturated acids were examined for acids of the higher degree of unsaturation, those with three and four double bonds. They contained relatively large amounts of a 4-bond acid, probably arachidonic, but no appreciable amount of 3-bond acid. The amount of 4-bond acid was greatest in the brain, next in the liver and kidney, then lung, then pancreas.

P. H. P.

Highly Unsaturated Fatty Acid of Liver Lipids. Preparation of Arachidonic Acid. J. B. Brown. (*J. Biol. Chem.*, 1928, **80**, 455-460.)—Experiments have been carried out with two objects, (1) to verify the presence of arachidonic acid in the lipids of liver, and (2) to isolate a specimen of the pure acid. As regards the first, the methyl esters of the fatty acids of liver lipids were prepared and fractionated into four fractions, and each fraction was analysed. The bromides of each fraction were found to contain practically the same amount of bromine, the results in each case being very close to the theoretical for methyl octobromoarachidate. As regards the second, the combined bromides of the several fractions were reduced with zinc in neutral alcohol, and practically pure methyl arachidonate was prepared. From this ester the acid was obtained by saponification. Some oxidation took place during the saponification, and the final product of iodine number 316 (theory 334) represents the purest specimen so far obtained. The results indicate therefore that arachidonic acid is the sole highly unsaturated fatty acid present in appreciable quantities in the lipids of pig liver. It occurs to the extent of 2.0 to 7.7 per cent. of the total fatty acids, depending on the method of calculation. The arachidonic acid obtained was a light amber oil, less mobile than the ester, and with a distinct fishy odour. The properties of methyl octobromoarachidate, methyl arachidonate and arachidonic acid are described.

P. H. P.

Oxidation of Lignoceric Acid. F. A. Taylor and P. A. Levene. (*J. Biol. Chem.*, 1928, **80**, 609-613.)—When cerebronic acid was oxidised to the next lower unsubstituted fatty acid, instead of pure lignoceric acid being obtained, a product was isolated that appeared to be a mixture of acids. It was therefore decided to determine whether an α -hydroxy acid of known purity related structurally to cerebronic acid could be degraded by oxidation, under similar conditions to those applied to cerebronic acid, to the next lower acid of the series, in good yield and uncontaminated by substances that could not be separated easily. Lignoceric acid was converted into its next lower homologue by passing it through the following steps (Levene and West (*J. Biol. Chem.*, 1913-14, **16**, 475)):



These reactions were partly carried out by Meyer, Brod and Soyka (*Monatsh. Chem.*, 1913, **34**, 1113), and by Levene and Taylor (*J. Biol. Chem.*, 1922, **52**, 227), but since it has recently become known that some higher aliphatic substances change on standing and cannot be brought back to their original melting points, and since the materials used by Levene and Taylor had stood for some time, it was decided to check their figures. The new experiments show that the melting points recorded by each group of workers should be increased, as shown by the following table:

	Meyer, Brod and Soyka. °C.	Levene and Taylor. °C.	Taylor and Levene. °C.
α -Bromolignoceric acid	68-69	68.5	69.5-70.5
α -Hydroxylignoceric acid	91-92	91-92	94-95
Isotricosanoic acid	—	73.5	76.5-77.5

Oxidation of α -hydroxylignoceric acid evidently gives rise to a single substance, isotricosanoic acid. The crude acid melted at 75–77° C., and the best specimens at 76.5–77.5° C. Further evidence is given in favour of the view of Meyer, Brod and Soyka that lignoceric acid is not a normal acid, for in this series the acid with an odd number of carbon atoms melts at a point between the melting points of the two adjacent even-numbered acids.

P. H. P.

Loosely-Bound Sulphur in Egg Albumin. W. D. Treadwell and W. Eppenberger. (*Helv. Chim. Acta*, 1928, 11, 1035–1042.)—Fresh egg-white was extracted with boiled water and filtered, and 20 c.c. of the extract heated with 20 c.c. of a 0.1 *N* solution of sodium hydroxide in a thermostat maintained at 78° C. by means of boiling alcohol. Air was excluded to avoid oxidation, the apparatus being arranged so that the operations were carried out in an atmosphere of nitrogen. The excess of alkali was then neutralised with 0.1 *N* hydrochloric acid, and the sulphide ions produced in the partly hydrolysed solution were titrated electrometrically with a 0.002 *N* solution of lead nitrate against a silver and silver chloride electrode. A 0.01 *N* standardised solution of sodium sulphide was used for comparison purposes, and was found to keep well in an atmosphere of nitrogen. This controlled hydrolysis gave hydrolysis-curves which indicate that the reaction is bimolecular and is finished after 3 hours, 0.266 per cent. of sulphide sulphur being found in the egg albumin. If this constitutes one-sixth of the total sulphur, the latter would comprise 1.616 to 1.520 per cent. of the protein molecule, the molecular weight of which would then be about 12,000.

J. G.

Volumetric Method for the Determination of Protein Solutions. W. D. Treadwell and W. Eppenberger. (*Helv. Chim. Acta*, 1928, 11, 1053–1062.)—A volume of the solution corresponding with about 30 mgrms. of protein is precipitated with about 200 mgrms. of the purest tannin (free from gallic acid) in the form of a 0.5 or 1 per cent. solution, and the mixture diluted to 100 c.c., shaken, and allowed to settle. A solution of Prussian blue (prepared by the addition of 25 c.c. of 0.2 *N* potassium ferrocyanide solution to 18.8 c.c. of 0.2 *N* ferric chloride solution, and dilution to 500 c.c.) is then added from a burette, the end-point being reached when a faint blue colour is imparted to the supernatant liquid after it has been centrifuged for 5 minutes (2,000 revolutions). At this point the albumin, which is a positive colloid, has completely adsorbed the negatively-charged Prussian blue, and 1 grm. of gelatin and egg-albumin may be taken as equivalent to 2.3 and 1.1 millimols of ferrocyanogen, respectively, the proportions of Prussian blue (*B*) and egg-albumin (*E*) or gelatin (*G*) being related by the equations $B = 0.915 \times E^{0.688}$ and $B = 1.92 \times G^{0.688}$ respectively. The end-point is unaffected by the presence of amino-acids, but inorganic salts should be removed by dialysis, and the acidity of the medium should be adjusted approximately to the P_a value corresponding with the iso-electric point of the substance concerned (gelatin 4.7, egg-albumin 4.8). The adsorbed colour is deepest in the case of gelatin, but egg-albumin gives more reproducible results, particularly if a standard of known strength is used for comparison purposes.

J. G.

Further Application of the Vanillin and Hydrochloric Acid Reaction in the Determination of Tryptophane in Proteins. I. Kraus Ragins. (*J. Biol. Chem.*, 1928, 80, 543-550.)—The author criticises the attack made by Looney (*J. Biol. Chem.*, 1926, 69, 519; ANALYST, 1926, 51, 588) on a previous paper by her (Kraus (*J. Biol. Chem.*, 1925, 63, 157; ANALYST, 1925, 50, 246)) on the vanillin and hydrochloric acid reaction for tryptophane, and states that it is "quite clear that he has not read the paper sufficiently carefully to warrant his generalised conclusions." A slight modification in the procedure of the reaction is now described, which has been devised to save time and material. The reaction is allowed to take place in the centrifuge tube instead of the precipitate being transferred to a flask, and a 0.2 mgrm. standard is used in place of the 0.4 mgrm. standard described previously. For concentrations of tryptophane of less than 0.2 mgrm., or for blanks, a known amount of tryptophane is added in order to insure quantitative precipitation. The vanillin and hydrochloric acid reaction applied directly to sixteen highly purified proteins gave very unsatisfactory results, as previously, but when the same proteins were first hydrolysed by trypsin and the indirect vanillin and hydrochloric acid reaction applied (which means precipitation of tryptophane by mercuric sulphate under definite conditions) good results were obtained. The filtrate from the mercury-tryptophane precipitate was shown definitely not to contain tryptophane. If peptide tryptophane is present in the mercury-tryptophane precipitate it reacts in the same way as free tryptophane with the vanillin and hydrochloric acid reaction. Proline or proline-containing proteins, such as gelatin, in the concentrations used by Komm (*Z. physiol. Chem.*, 1926, 156, 161) have no effect on the vanillin and hydrochloric acid colour reaction, but in higher concentrations a secondary colour forms which interferes with the true tryptophane colour. Chloride ion concentrations of 0.3 per cent. or higher interfere with the quantitative precipitation of tryptophane by mercuric sulphate, whilst sodium ion concentrations up to 2 per cent. have no effect. Thus sodium is not a factor in retarding the precipitation of tryptophane by mercuric sulphate in a pepsin-hydrochloric acid medium.

P. H. P.

Colorimetric Determination of Inorganic Sulphate in Small Amounts of Urine. B. S. Kahn and S. L. Leiboff. (*J. Biol. Chem.*, 1928, 80, 623-629.)—A colorimetric method is described for the determination of inorganic sulphate in small amounts of urine. The inorganic sulphate is precipitated as benzidine sulphate. The precipitate is then diazotised and coupled with phenol in an alkaline medium to produce a yellow colour which is proportional to the amount of benzidine. This is compared in a colorimeter with a similarly treated standard sulphate solution. Phenol was found to be the ideal reagent for colour development. It forms a dye which is soluble in aqueous solutions, highly stable, and whose tinctorial power does not demand excessive dilutions. An excess of phenol has no effect upon the colour development, but an excess of alkali retards it. When known amounts of sulphur in the form of sulphate were added to urine very good recoveries were obtained. The method was checked against a gravimetric method, and the results obtained are tabulated.

P. H. P.

Highly Accurate Method for the Analysis of Urea. M. Taylor. (*J. Amer. Chem. Soc.*, 1928, **50**, 3261–3265.)—Being a non-electrolyte of low equivalent weight and chemically indifferent, urea forms an excellent reference substance for use in physico-chemical and colloidal problems. It may be determined with an accuracy of 0.02 per cent. by conversion into ammonia and carbon dioxide by the action of hydrochloric acid in an autoclave. This reaction proceeds to completion in presence of a very slight excess of the acid, and, as the latter does not vaporise under the conditions used, distillation of the resulting ammonia with soda is not necessary. The digestion is carried out in a 500 c.c. stoppered conical Pyrex or silica flask provided with an exit tube of inverted U-shape sealed in or near the top of the flask. The flask is weighed, and the urea solution and standard acid are pipetted into it, the weight being noted after each addition. A Pyrex test-tube, containing a little water into which the side-tube dips, acts as scrubber to the escaping carbon dioxide, this being absorbed by the distilled water, containing a few c.c. of soda solution, in the autoclave. Subsequent expulsion of the carbon dioxide by aeration or boiling of the reaction mixture is then unnecessary. The flask and scrubber are covered with tinfoil while in the autoclave, and, after the air has been displaced and the heating continued for 30 minutes at 2 atmos., and for 4 hours at 4 atmos., the autoclave is allowed to cool. The glass stopper of the flask is then removed and replaced by a rubber bung carrying a tube, by means of which the contents of the scrubber are sucked back, and the scrubber rinsed several times into the flask. The excess of acid is titrated with soda solution after addition of two drops of 0.02 per cent. methyl red solution. T. H. P.

Urobilin Content of Normal Human Blood. M. A. Blankenhorn. (*J. Biol. Chem.*, 1928, **80**, 477–485.)—Although the physiology of urobilin deals indirectly with blood urobilin, the normal urobilin content of human blood has not before been described, and there has been no method for its determination. Most urobilin studies have been made either with the Schlesinger fluorescence method or with the Ehrlich test. Of these, the latter is not very sensitive whilst the Schlesinger test is very sensitive (0.0048 mgrm. per 100 c.c.) and highly specific; Elman and McMaster (*J. Exp. Med.*, 1925, **41**, 503) have made it quantitative by the development of a standard. A method for blood urobilin is now described by the author. It consists in the application of the fluorescence test to blood serum modified to make it more sensitive by refinements in two main directions; namely, to provide absolutely clear supernatant solutions in which to develop fluorescence, and to examine these solutions in a dark room with an intense beam of light. The fluorescence is then measured quantitatively by means of the Elman and McMaster standard prepared by a simplified technique. Details of the method are given, together with illustrations of the lamp and apparatus used for comparison of the solutions with the standards. The standard used is a dilute aqueous solution of neutral acriflavine in a series of concentrations, the strongest of which is a solution of 1 part in 10,000,000, and the weakest a solution of 1 part in 200,000,000. A chart is given which is arranged for direct determination of urobilin values. With

this method it has been possible to detect fluorescence in practically every normal human blood. Of 128 specimens of human blood presumably normal, but two were negative, and in twelve instances no test could be made owing to inability to clear the specimens. Probably with greater experience none will be found negative, and with good technique there should be very few with which no test can be made. The average of a series of 107 normals gives 0.28 mgrms. of urobilin per 100 c.c.; this may be slightly greater than is justifiable, as a few may have been slightly abnormal specimens. Numerous pathological specimens were measured which gave results as high as 33 mgrms. per 100 c.c., the highest values being in patients with nephritis, malaria, pneumonia, and tuberculosis with fever; one patient with complete obstruction of the gall duct and with complete intestinal acholia was clearly negative. This agrees with current ideas of urobilin metabolism.

P. H. P.

Organic Analysis.

General Method for the Micro-Determination of Carbon by the Use of Chromic Acid Oxidation. A. Bolvin. (*Comptes rend.*, 1928, **187**, 1076-1079.)—The carbon content of an organic substance may be accurately determined by subjecting a portion, weighed on the microbalance, to chromic acid oxidation in the presence of sulphuric acid and silver dichromate in a boiling water bath for half an hour. Nicloux's apparatus (*Compt. rend.*, 1927, **184**, 890) is used, modified so that any carbon monoxide that may be produced is burnt by an electrolytically heated platinum wire in the bulb containing the potassium hydroxide. The method is universally applicable, and, by weighing the precipitates on special small Pregl filters, the proportion of carbon may be calculated without using a microbalance. The method is regarded as nearly as accurate as Pregl's method. Such substances as graphites, osazones, picrates, alkaloids, silicotungstates, and mercury compounds were satisfactorily analysed.

D. G. H.

Physical Properties of Pure Triglycerides. R. B. Joglekar and H. E. Watson. (*J. Soc. Chem. Ind.*, 1928, **47**, 365-368T.)—Various pure triglycerides have been prepared by a modification of Bellucci's process, a mixture of three molecules of glycerol and one of the acid being heated to 180° C. and the temperature gradually raised to 215° C. during 2 hours at 30-40 mm. pressure, then to 250° C. in 1 hour; this temperature was maintained for 1 hour, while the pressure was reduced to 6 mm. The crude products were crystallised six or seven times from concentrated alcohol and recrystallised from light petroleum and ether, the last traces of solvent being expelled at 100° C. under reduced pressure. The melting point and refractive index are of little value as criteria of purity, and the densities, viscosities, and solidification points vary appreciably even when a fair degree of purity is attained. The viscosity appears to be the most sensitive test for impurity, but its determination requires very careful temperature adjustment, and for practical testing the solidifying point is almost as accurate, and far easier to measure. As regards the complex nature of the solidification of the

triglycerides, it is sufficient to regard these as existing in two forms, the β -form obtained by crystallisation from solvents, and the α -form by heating the β -form to its melting point, which appears to be a transition temperature. When a triglyceride is cooled, crystallisation does not occur without seeding until the solidification point of the α -form is reached. In the neighbourhood of this temperature, once crystallisation has started, the transformation $\alpha \rightarrow \beta$ takes place in a few minutes, and results in resolidification. Consistent values are obtainable if 3 grms. or more are introduced into a 2 cm. tube surrounded by an air-jacket immersed in a bath, the temperature of which is raised during the experiment so as to be not more than 4° C. below that of the substance. Stirring has no effect with tristearin, but should be adopted with the lower members, as it reduces the time required for the temperature rise. The lower melting point (2) is taken as the temperature of initial softening in a capillary tube with a temperature rise of about 1° C. per minute, and the higher (1) as the temperature of complete liquefaction under similar conditions. The results obtained are summarised in the following table:

	Caprin.	Laurin.	Myristin.	Palmitin.	Stearin.
Melting point (1)	31·6	46·2°	56·5°	65·6°	71·8° C.
" (2)	—	18·0°	33·0°	46·2°	55·0° C.
Solidifying point	30·3°	45·3°	56·1°	65·2°	71·3° C.
Viscosity at 70° C.	0·0688	0·1030	0·1342	0·1679	0·1850(75°C)
	60° C.	60° C.	60° C.	80° C.	80° C.
Refractive index at °	1·4370	1·4402	1·4428	1·4376	1·4395
Density at °	0·9059	0·8943	0·8860	0·8663	0·8632
Surface tension	27·3	27·9	28·7	27·6	28·1

For tristearin-tripalmitin mixtures containing from 25 to 50 per cent. of tristearin double solidification points may be observed, but this has not been found with other mixtures. The complete higher solidification curve, unlike that for the corresponding acids, is characteristic of a simple mixture. The refractive index of tristearin-tripalmitin mixtures is a linear function of the composition at both 70° and 80° C. The density, viscosity and surface tension of these mixtures present no unusual features.

T. H. P.

Determination of Neutral Oil in Sulphonated Oils. Committee Report. G. W. Priest. (*J. Amer. Leather Chem. Assoc.*, 1928, 23, 599.)—Three samples of sulphonated oil prepared in the laboratory were analysed in three laboratories for their neutral oil content by five different methods:—(1) The official method of the American Leather Chemists' Association which necessitates a complete analysis (*J. Amer. Leather Chem. Assoc.*, 1920, 283). (2) Lewkowitch's method, in which 30 grms. of the oil are dissolved in 50 c.c. of water, and 20 c.c. of ammonia and 30 c.c. of glycerin are added, the mixture being extracted with two portions of 100 c.c. each of ether. The ethereal extract is washed, evaporated and dried to constant weight. (3) The same method as No. 2, but with the use of only 10 grms. of the oil. (4) The same method as No. 3, but with petroleum spirit used instead of ether. (5) Ten grms. of the oil are dissolved in 50 c.c. of water. Fifty c.c.

of alcohol are added, and the mixture rendered neutral to phenolphthalein with $N/2$ potassium hydroxide solution. The mixture is extracted three times with petroleum spirit, the mixed extracts being washed, evaporated and dried to constant weight.

All three laboratories condemn method No. 1 as giving excessively high results in neutral oil content. One laboratory recommends method No. 2 until further research shows which solvent is the best. The other laboratories recommend method No. 5 as giving by far the best separation of the emulsion and the clearest solutions, but not necessarily the most accurate results. There was difficulty in drying the neutral oils to constant weight, as they did not become constant after 23 weighings covering a period of 30 days, the losses in weight varying between 25 and 5 per cent.

R. F. I.

The Cold Test for Neatsfoot Oils. A. C. Orthmann and W. J. Arner. (*J. Amer. Leather Chem. Assoc.*, 1928, 23, 595.)—The test described was devised to overcome the inaccuracies of existing methods, in which the low temperature obtained by the use of the usual freezing methods is uncontrollable. In this new method the low temperature is obtained by passing dry air through ether contained in a Dewar flask. A test-tube, 23 cm. long \times 1.5 cm. internal diam., is filled to a depth of 3 cm. with the oil. The tube is provided with a rubber stopper through which a special long-stemmed thermometer passes, reaching to just below the surface of the oil, the scale being wholly above the rubber stopper. The long test tube is inserted in another rubber stopper (with 3 holes) fitting the 3-walled Dewar flask, and provided with two tubes for the aspiration of dry air through the ether with which the Dewar flask is three-quarters filled. The initial temperature of the oil is that of the laboratory, and when the temperature has fallen to about 10° C. above the expected pouring point, observations are made at each degree, the whole apparatus being tilted to see whether or not the oil still flows. The "pour-point" is taken as 1° C. above the point at which the oil ceases to flow. The cloud-point is also easily obtained, since the whole apparatus is transparent.

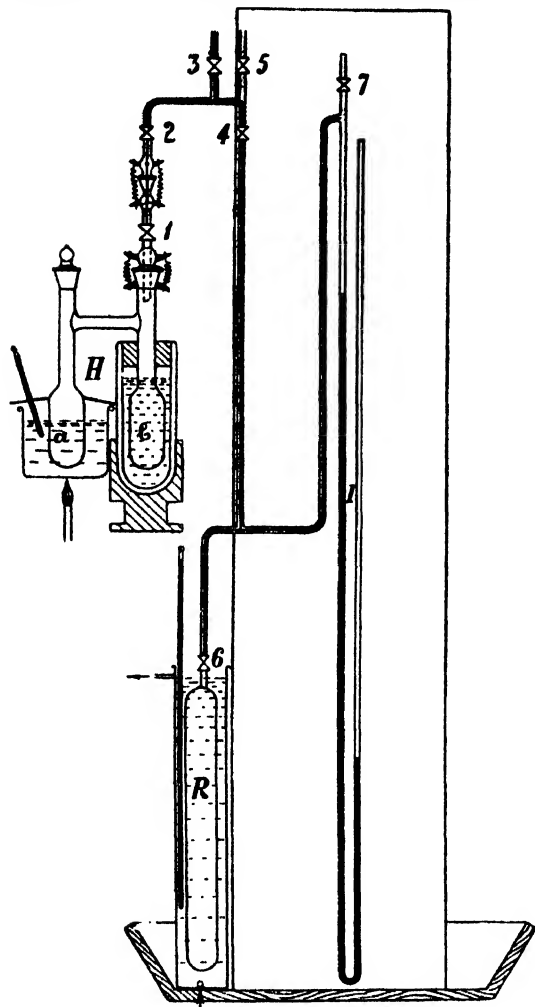
Tests carried out on a number of oils by this method and by that proposed by the American Society of Testing Materials showed good uniformity, but the new method is much simpler and more rapid. The apparatus is obtainable from Messrs. Carl Stelling, Hamburg.

R. F. I.

Note by Abstractor.—In the discussion which followed the paper several speakers expressed the view that the Cold Test for Neatsfoot Oils is obsolete.

Determination of the Hydrogen Value of Unsaturated Compounds. H. I. Waterman, J. N. J. Perquin and H. A. van Westen. (*J. Soc. Chem. Ind.*, 1928, 47, 363–365T.)—The procedure described represents an attempt to devise a more widely applicable method than that of Grün (*Die Analyse der Fette und Wachse* 1925, p. 188) for determining the hydrogen value of unsaturated compounds, including those with high vapour pressures at the ordinary temperature. The catalyst used consists of active palladium on norit or carboraffin as support,

and is prepared by Kaffer's method (*Ber.*, 1924, 57, 1263), the reduction being effected by hydrazine sulphate. The catalyst is prepared to contain 10 per cent. of palladium, calculated on the air-dry carbon. The hydrogen used is freed from oxygen by passage over a red-hot platinum star, then dried by concentrated



sulphuric acid, and finally led through a vessel placed in liquid air. The gas is brought, *via* the taps 5, 4 and 6, into the evacuated vessel R (about 1600 c.c.), which is carefully calibrated beforehand by weighing full of water. This calibration may be controlled by removing part of the hydrogen with a Töpler high-vacuum pump working automatically, the pressure and temperature of the gas in R, surrounded by a water-jacket, being determined before and after the suction. This method gave 1586.5 c.c., and the weighing method 1588.2 c.c., for the capacity of R at 0° C. The hydrogenation apparatus H, evacuated beforehand, is now filled with a known volume of hydrogen by opening taps 1 and 2, reading the pressure on the manometer, and then closing 1 and 2. The catalyst (2 grms.), freed from gas by being heated in an oil-bath at about 200° C. under constant pumping (1 hour usually sufficient), and previously introduced into tube *a*, and tube *b*, containing a weighed amount of the unsaturated substance, having been placed in liquid air, vessel H, including the tubes up to tap 6, is pumped wholly free from air.

Before the commencement of the hydrogenation the vessel *a* is cooled with liquid air, so that the substance in *b* distils from *b* to *a*, *b* not being cooled during this operation. Then, after introduction of a known volume of hydrogen, the hydrogenation starts and may be accelerated by shaking vessel H, which is separated from the apparatus after taps 1 and 2 have been closed. After hydrogenation, the tube *a* is cooled with liquid air, and the vessel H is completely evacuated after being reconnected, the residual hydrogen, including that between taps 1, 2, 3, 5, and 6, being pumped through a coil cooled with liquid air into a special measuring tube by the Töpler pump.

The reaction product, if volatile, is now passed into *b* by placing the liquid air cooling vessel round *b* and no longer cooling *a*, which is finally heated in an oil-bath to about 200° C., in order to add any hydrogen adsorbed by the catalyst to the quantity in the measuring tube. The weight of the volume of the hydrogen used in the hydrogenation is calculated and expressed as per cent. of the unsaturated compound taken. The maximum error seems to be about 5 c.c. of hydrogen, or ± 0.5 mgrm. The duration of the contact between catalyst, substance and hydrogen has been taken at about 15 mins., but this may possibly be lessened. The following hydrogen values were obtained by this method: cyclohexane, practically nil; benzene, 0; amylene, a value equal to that calculated from the known bromine value.

T. H. P.

Two New Methods for Determining Phenol in Waste Liquors. H. Dehe. (*Chem. Ztg.*, 1928, **52**, 983–985.)—The phenol in waste liquors from gas-works, etc., may be determined by the two following methods:—To 200 c.c. of the well-mixed liquor are added 10 c.c. of saturated zinc acetate solution, 40 c.c. of 5 per cent. silver nitrate solution (if much hydrocyanic or thiocyanic acid is present, a greater volume of the silver nitrate or a more concentrated solution must be used), and 10 c.c. of dilute sulphuric acid (1 : 3), the containing flask being left for 3–5 hours with occasional vigorous shaking. One-half of the total volume is then filtered, and the filtrate acidified with dilute sulphuric acid, treated with a few drops of 3 per cent. hydrogen peroxide solution, and distilled until the distillate fails to respond to the test for phenol with Millon's reagent and nitric acid. The total distillate is rendered strongly alkaline with concentrated sodium hydroxide and evaporated, the cold residue being transferred to a 500 c.c. flask and made up to volume.

(1) *Iodimetric determination.*—Ten c.c. (or more if little phenol is present) of this solution are heated to 50–60° C. with water and treated with 15 c.c. (more if the phenol-content is high) of 0.1 *N* iodine solution, allowed to cool, acidified with about 15 c.c. of diluted sulphuric acid (1 : 3), and titrated with 0.1 *N* thio-sulphate solution (1 c.c. of 0.1 *N* iodine corresponds with 1.567 grm. of phenol).

(2) *Fractional titration.*—About 55–60 c.c. of the distillate made up, as above, to 500 c.c., are left for a few minutes in a closed Erlenmeyer flask with as much solid baryta as will lie on the point of a knife, the flask being shaken occasionally. After removal of the precipitate by filtration, 25 c.c. of the filtrate are treated with about 10 drops of dilute sulphuric acid (1 : 3), the barium sulphate being filtered off and washed two or three times with as little carbon dioxide-free water as possible. If any barium sulphate passes the filter, the filtrate is returned to the filter before the latter is washed. Exactly 0.2 c.c. of 0.1 per cent. alizarine yellow solution is then added, and the P_H of the solution adjusted to 11.04 by means first of strong sodium hydroxide solution and dilute sulphuric acid and afterwards of 0.1 *N* sodium hydroxide and 0.1 *N* acid, use being made of a buffer solution consisting of 50 c.c. of 0.1 *N* sodium hydroxide and 3 c.c. of 0.1 *N* hydrochloric acid. Exactly 0.1 c.c. of 1 per cent. phenolphthalein solution is next added, the solution being

titrated to $P_n = 8.4$, with the help of a buffer solution containing 62 c.c. of borate solution (12.404 grms. H_3BO_3 and 10 c.c. of 0.1 *N* sodium hydroxide, made up to 1 litre with water free from carbon dioxide) and 38 c.c. of 0.1 *N* hydrochloric acid. From the volume of 0.1 *N* acid used, the correction for pure water is subtracted; 1 c.c. of 0.1 *N* acid corresponds with 9.4 mgrms. of phenol or, if the above conditions are observed, the number of c.c. of 0.1 *N* acid, when multiplied by 2.09, gives the number of grms. of phenol per litre of the waste liquor. If the latter contains less than 4 grms. of phenol per litre, the 500 c.c. of distillate is evaporated to 250 c.c., the factor then becoming 1.045.

T. H. P.

Determination of Ionone. R. D. Hendriksz and A. Reclaire. (*Perf. and Ess. Oil Rec.*, 1928, 19, 493.)—Five c.c. of the ionone are heated under a reflux condenser for two hours with a mixture obtained by dissolving 15 grms. of hydroxylamine hydrochloride in 37.5 grms. of water, adding 18 grms. of potassium hydroxide dissolved in 37.5 grms. of water, and, if necessary, filtering. After the boiling, the liquid, as hot as possible, is poured into a separating funnel, the aqueous layer being run off and the oximated oil washed thrice with hot brine and filtered as hot as possible (in a little drying oven at 100° C.). The nitrogen in about 0.5 to 1 gm. of the oximated oil is determined by the Kjeldahl-Gunning method (see *ibid.*, 1927, 18, 130; 1928, 19, 143), the oxidation being usually complete in 2–3 hours. If *a* is the number of c.c. of 0.2 *N* sulphuric acid required per 1 gm. of the oil, the percentage of ionone in the sample is given by $53.82 a / (14 - 0.042 a)$.

T. P. H.

Inorganic Analysis.

Precipitation of Lead by *o*-Oxyquinoline. V. Marsson and L. W. Haase. (*Chem. Zeit.*, 1928, 52, 993–995.)—Lead is precipitated as flocculent, yellow oxyquinolate by addition of a cold saturated aqueous solution of the reagent to the feebly ammoniacal solution. The excess of ammonia is expelled by boiling after the precipitation, the precipitate collected after 12 hours' standing in the cold, washed with a minimum of water, dried, and weighed; lead factor, 0.4185. The precipitate has a certain solubility, which is decreased to 0.004 gm. per litre by the employment of 10 times the quantity of reagent required for precipitation.

W. R. S.

Determination of Vanadium in Steel. K. Swoboda. (*Chem. Zeit.*, 1928, 52, 1014–1015.)—The sample (2 grms.) in a 500 c.c. flask is dissolved in warm sulphuric acid (1 : 6; 50 c.c.), the loss of water being made good. The boiling solution is oxidised with nitric acid, drop by drop, and an excess of 5 c.c. added; the red fumes are boiled off. Fifty c.c. of 10 per cent. ammonium persulphate are added; boiling is continued for some minutes, and again after addition of ammonia in excess. After the heat is removed, 50 c.c. of ammonium persulphate, and 100 of ammonium molybdate solution, as used for the phosphorus determination, are added. The precipitate is dissolved in strong nitric acid, tungstic

acid remaining in solution ; the clear boiling solution is precipitated by portions of 3 to 4 drops of 10 per cent. sodium phosphate solution at intervals of 20 seconds, until the colour of the precipitate changes from dark orange to pale yellow-orange (10 to 40 drops in all). The change marks complete vanadium precipitation by the formation of the yellow phosphomolybdate. Boiling is continued until the liquid is very concentrated ; the precipitate is then collected and washed with a solution of 20 c.c. of ammonia (0.91) and 25 c.c. of strong sulphuric acid per litre. Filter and precipitate are returned to the flask and heated with 50 c.c. of nitric, 5 c.c. of phosphoric, and 50 c.c. of sulphuric acid (all strong). When the paper has been oxidised, the solution is evaporated until it fumes. After cooling, dilution with water, oxidation with permanganate, and renewed cooling, 50 c.c. of hydrochloric acid (1:1) are added, and the solution boiled down until it fumes copiously. The cold mass is taken up in 250 c.c. of water, and the blue solution is heated to 80° C. and titrated with permanganate. $V=0.915 \text{ Fe}$.

W. R. S.

Precipitation of Tungsten as Mercurous Tungstate. V. Spitzin. (*Z. anal. Chem.*, 1928, **75**, 433-440.)—The precipitation of sodium tungstate solutions by mercurous nitrate was investigated. The solution is made neutral to methyl orange with nitric acid, boiled, and precipitated with an excess of a solution of mercurous nitrate (the salt dissolved in water without addition of nitric acid ; solution kept over metallic mercury). The precipitate is washed as usual and ignited in porcelain without the use of a blast burner. Quantitative results are thus obtained without subsequent addition of alkali. If, however, the solution is acid before precipitation and afterwards neutralised by alkali, the recovery is not quantitative ; the explanation advanced is that mercurous tungstate is decomposed by nitric acid into free tungstic acid and mercurous metatungstate, which is soluble.

W. R. S.

Use of Potassium Iodate in Back Titration for the Determination of the Hypochlorite Content of Solutions. J. R. Lewis and R. F. Klockow. (*J. Amer. Chem. Soc.*, 1928, **50**, 3243-3244.)—In the determination of hypochlorite by means of arsenite, thiosulphate, or iodide solution, the excess of these reagents may be determined by titration with potassium iodate. (1) A measured volume of the hypochlorite is added to a known volume in excess of standard arsenite solution, the unused arsenite being then titrated with 0.1 N iodate solution in presence of at least 12 per cent. hydrochloric acid ; the results thus obtained are accurate in presence of small proportions of nitrate or chlorate, (2) The hypochlorite is added to the acid or neutral thiosulphate solution, the liquid being then cooled in an ice-bath and titrated with iodate solution ; in this case the results are not concordant if chlorate is present. (3) When the hypochlorite is reduced by potassium iodide the mixture is cooled in ice-water before titration with iodate ; here, too, chlorate vitiates the results.

T. H. P.

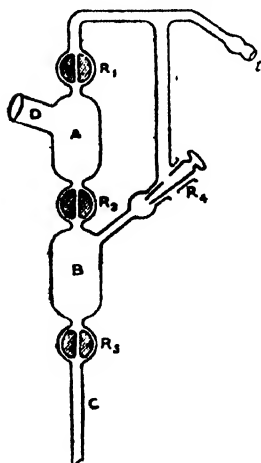
Physical Methods, Apparatus, etc.

Colour-Measurement of Tanning Extracts. M. A. de la Bruere. (*J. Int. Soc. Leather Trades Chem.*, 1928, 12, 485.)—The tintometer usually employed for the colour-measurement of tannin extracts (that of Lovibond) is subject to a large personal error with different operators, and with the same operator under different conditions of light. The author finds that by photographing their absorption spectra the red and yellow glasses used allow rays of very varying wave-length to pass. For determining the colour of a solution he suggests the employment of a photo-electric cell coupled to a galvanometer. The rays from an iron arc lamp after passing through a condenser, a colour filter, and the solution under examination, act on a photo-electric cell forming part of a circuit embracing a battery and a galvanometer. Successive readings are taken with the test solution and with distilled water by means of various colour-filters, and the differences obtained are noted. A curve is then constructed, representing the colour of the solution examined, having for abscissae the colours in spectroscopical order, and for ordinates the ratio between the deviations obtained with the test solution and with water.

R. F. I.

Calorimetric Investigations. Benzoic Acid as a Standard for the Standardisation of Combustion Calorimeters. P. E. Verkade. (*Chem. Weekblad*, 1928, 25, 666–667.)—The author discusses the decision in 1922 of the International Union of Pure and Applied Chemistry to adopt as standard in the calibration of bomb calorimeters the value 6319.0 15° cal. for the heat of combustion of benzoic acid, corresponding with the isothermal heat of combustion of 1 gram. weighed *in vacuo* and burnt at 20° C. He concludes that this value differs but little from the true figure, though the results of other workers indicate that some difficulty may be experienced in maintaining a constant temperature of 20° C. during the experiment, and it is desirable that such experiments be arranged so that the mechanical equivalent of heat is not required for the calculation of the result in calories. The temperature coefficient is -0.238 cal./°C., and the factors 1.00084 and 1.00075 may be used to obtain the values when the benzoic acid is weighed in air with platinum and brass weights, respectively. The values in 15° cal. are tabulated for temperatures between 0° and 21° C.

J. G.



Separator for Fractional Distillation under Reduced Pressure. R. Delaby and R. Charonnat. (*Bull. Soc. Chim.*, 1928, 43–44, 1287–1288.)—The apparatus shown in the diagram consists of 2 bulbs, A and B, of about 60 c.c. capacity for ordinary laboratory work, the upper bulb being connected at D with the side tube of the distilling flask or the refrigerator. R_1 , R_2 , and R_3 are stop-cocks, R_4 is a stopcock allowing for the entrance

of air, and t connects with the vacuum pump. At the beginning of the distillation R_1 and R_2 are open, R_3 and R_4 shut, and the first fraction collects in A and runs into B. R_2 is then closed, air allowed to enter by R_4 , and the fraction run out through R_3 . During this time the second fraction is collecting in A. R_3 is then shut, followed by R_1 , to allow a vacuum to re-form in B, R_4 being turned to its original position, and immediately after R_1 is again opened. D. G. H.

Automatic Pipette. M. Hyman. (*J. Soc. Chem. Ind.*, 1928, 47, 3681.)—

The arrangement shown allows a large number of equal portions of a liquid to be measured out quickly and accurately. The stem of the pipette is cut off at the mark and is fitted, by means of a rubber stopper, into the wide tube D about 3 inches long. This tube is constricted at A, and is connected by rubber tubing ($1\frac{1}{2}$ inches long) with the glass tube C which serves as mouthpiece. The pipette is filled by suction until the liquid overflows into D. The rubber tubing is then compressed, the level of the liquid falling somewhat below the graduation mark. The mouthpiece is then closed with the forefinger and the rubber tubing released, with the result that the liquid rises again in the pipette and overflows. The pipette, held by the mouthpiece only, is now raised from the liquid and the contents are delivered into the receiving vessel, any necessary drainage time being allowed as usual. When the trap D becomes full of overflowing liquid, the rubber tubing and mouthpiece are removed, and the liquid is poured out.

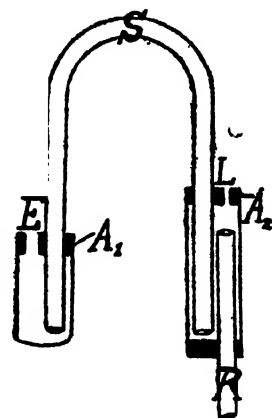
T. H. P.



Practical Siphon. H. Wentzel. (*Chem.*

Ztg., 1927, 52, 898.)—The siphon, which is particularly suitable when the rate of flow of liquid is to be controlled (*e.g.* in cooling vessels),

consists of an inverted U-tube S, the ends of which are held in wider tubes by the stoppers A_1 and A_2 . These are provided with holes E and L for liquid and air inlets, respectively, and R is an adjustable outlet tube.



J. G.

References to Scientific Articles not Abstracted.

COPPER IN ANTIQUITY. *Nature*, 1928, 122, 886 (Dec. 8).

A summary of the interim report of the British Association Research Committee on the sources of early Sumerian copper—Analyses of bronze from Ur—Egyptian bronze—Ancient ore.

THE PROTECTION OF ANIMAL FIBRES AGAINST CLOTHES MOTHS AND DERMESTID BEETLES. By C. O. CLARKE. *J. Text. Inst.*, 1928, 19, 295-320 (December).

Species of clothes moths—Life history—The Dermestidae—Methods of control—Sterilisation and fumigation—"Moth balls," etc.—Outline of patents—Methods of rendering the fibre moth-proof—List and outline of patents—References to the literature—Illustrative plates.

RECENT DEVICES FOR MEASURING THE FLOW OF AIR. By R. A. H. FLUGGE-DE-SMID. *J. Chem. Met. & Mining Soc., S. Africa*, 1928, 29, 82-95 (October).

Measurement of low velocities in mines—Measurement of high velocities—Pitot tube and manometer—Micromanometer—Measurement of the flow of compressed air—Correction for temperature.

Reviews.

LABORATORY MANUAL FOR THE DETECTION OF POISONS AND POWERFUL DRUGS.

By Dr. WILHELM AUTENRIETH, Professor in the University of Freiburg I.B.

Authorised translation by WILLIAM H. WARREN, Ph.D., Professor of Organic Chemistry in Clark University, Worcester, Mass. Pp. xxvi and 698. London: J. & A. Churchill. Price 30s.

Autenrieth's manual has now reached its sixth American edition, the translator being Dr. W. H. Warren. This work, we venture to suggest, should find a home on the shelves of every analyst who may be called upon to make toxicological investigations, and those who have to make assays of pharmaceutical preparations and liquids containing alkaloids will find many useful hints. The examination of blood stains is also included.

The manual is essentially practical, and is chiefly concerned with the chemical nature, isolation and estimation of poisonous substances, so that if detailed knowledge of symptomatology and lethal dose of a poisonous substance is required, other works will have to be consulted.

An examination of analytical methods described reveals that they are for the main part sound, and the worker following the technique advised should bring his investigation to a satisfactory termination. Full references are given to original papers, so that the bibliography may be looked up. The chief line of criticism that may be directed to this work is in the form of errors of omission rather than commission. To mention a few, there is no reference to the Hartridge reversion spectroscope for the estimation of carbon monoxide in blood, and we should have thought that the estimation of ethyl alcohol in blood and urine had assumed sufficient forensic importance to warrant inclusion. In the section on blood stains the valuable haemochromogen crystal test, as worked out by Takayama, should be mentioned.

The book contains two indexes, author and subject, both of which are extremely thorough.

G. ROCHE LYNCH.

HANDBUCH DER BIOLOGISCHEN ARBEITSMETHODEN, E. ABDERHALDEN. Abt. IV, ANGEWANDTE CHEMISCHE UND PHYSIKALISCHE METHODEN. Teil 8, Heft 9. DIE REFRAKTOMETRISCHE UNTERSUCHUNG DER MILCH. By E. REISS. Berlin: Urban and Schwarzenberg, 1928.

Those workers who, interested in the attention which has recently been given to the use of the refractometer in milk analysis in this country, turn to this book for full information on the subject will be disappointed. It is a small pamphlet, containing in all some twelve pages of text, although the title-pages, tables of contents, and index of the whole volume, of which this forms a part, are included. The index extends to forty pages, each of three columns, so that this section will be necessary for all those who have the remainder of the volume.

Of the twelve pages of text, six and a half are taken up with figures and tables. One page contains a description of the instrument and introductory remarks, whilst an adequate description of the determination of fat in milk and cream occupies three pages, although this is a process which is not likely, in view of the accurate and convenient mechanical methods now available, to be used to any extent in this country. One page contains an outline of the methods used for the determination of the refraction of milk serum, whilst the determination of lactose by similar means completes the story in about half a page.

It is a little difficult to see of what use such an outline can be to anyone. To those experienced in such methods the almost complete absence of guides to interpretation and the sketchy method of treatment throughout will prove particularly irritating, whilst those seeking their first knowledge of the subject in these pages may easily be misled into thinking that the various processes described yield far more definite information than they actually do.

As so much work has been done on this subject in Germany, it seems strange that the opportunity afforded to the writer, of collecting together the available information, has not been utilised to a much greater extent. This section will be of no assistance to those who wish to decide for themselves what legitimate value the refractometer has in milk analysis.

G. D. ELSDON.

PHOTOCHEMICAL PROCESSES. By GEORGE B. KISTIAKOWSKI, Research Associate in Chemistry, Princeton University. American Chemical Society Monograph Series. New York: The Chemical Catalog Company, Inc. 1928. Price \$5.50.

The kinetics of photochemical reactions has been treated in this book from the standpoint of the quantum theory. In an introductory chapter the author briefly examines the theories of the primary process accompanying the absorption of light by molecules, and the mechanism of the resulting chemical change. Then follow chapters on the Einstein Equivalence Law, Chain Reactions, Photosensitisation, Catalysis and Inhibition, and the Effect of Temperature and the Frequency of Radiation on the Rate of Photochemical Reactions.

The author has accomplished the very difficult task of co-ordinating a mass of heterogeneous information into a highly readable book. This has been done without the sacrifice of detail, which makes it still more remarkable. The experimental data have been subjected to a detailed examination, and the author has dealt with contradictory evidence in a critical manner. The skill with which he has analysed the information available on photochemical processes has added very largely to the value of the book.

If there be any point of criticism that can be raised, it is that the introductory first chapter is too condensed for a student reading the book for the first time. This chapter might with advantage be treated at more length, and in a more elementary manner.

The author is to be congratulated on a good, clear account of the basis of photochemistry which takes the subject further than any previous text-book on the subject.

W. E. GARNER.

GLYCEROL AND THE GLYCOLS. By J. W. LAWRIE, Ph.D. Pp. 447. New York: The Chemical Catalog Co., Inc. 1928. Price \$9.50.

This volume is one of the American Chemical Society's series of monographs; its author is a research chemist with the Du Pont Co., and he obviously has experience of the glycerin industry. There is no other volume, so far as the reviewer is aware, which concentrates so much information on glycerin; it is almost an encyclopaedia of the published work on either glycerin or ethylene glycol; there are but few important papers which are not noted. This fact is a distinctive merit, but also has disadvantages, for one finds that it is so encyclopaedic that it is not critical. On each subject there are described many methods, whether it be of manufacture, distillation, or analysis, but the critical faculty is lacking; there is no indication which process is to be recommended, and some are of no real value or importance.

After a short historical chapter, there follow about 100 pages describing processes of saponification, evaporation and distillation; not much is novel, but all the more modern types of multiple effect evaporators are carefully described. Then there is a 50-page chapter on fermentation glycerin; this is particularly interesting, because it is less well known; all the patented processes are described, but again without sufficient criticism, as some are not of any great merit. The difficulties of purification and the need of extra distillation are not quite sufficiently brought out here; the optimistic statements of inventors or patentees are cited, often without comment. To read all these one would almost think that fermentation glycerin, instead of being unable to compete with the product of the soap works, was an established manufacture; it certainly is not in Europe, despite its importance to Germany during the War. Chapter VI collects the published data on physical properties, both the common and uncommon ones.

Chapters VII and VIII give the chemical reactions of glycerol, and IX and X its quantitative determination. These chapters seem to the reviewer the weakest, for they give methods without comment and end with tables showing erroneous results; these are to illustrate the difficulties of glycerin analysis, but really they only show bad working; analyses of crude glycerin which only add up to 96 to 99 per cent. are manifestly wrong, and could only be passed out by a blunder; they are not representative. It is possible to check the results of glycerin analyses by addition and specific gravity calculations so as to eliminate such errors; so, apart from human fallibility, which makes occasional blunders escape the most systematic checks, these should not appear. The main causes of differences in glycerin analyses when they do arise, which is not frequently, is the sampling in the presence of settled salt. The method for water estimation (p. 296) is older than stated; it was worked out many years ago by R. G. Grimwood.

Chapters follow on commercial utilisation, production and prices, and on nitro-glycerin; perhaps the last is better dealt with in books on explosive manufacture. Chapter XIV is of interest; it treats of the manufacture of ethylene glycol and its properties, advantages and disadvantages. Lastly, there is a brief prophecy (Chap. XV) of the probable future of the industry which is of particular interest, as the publication coincides with a period of acute depression in the glycerin trade. Dr. Lawrie does not make a very cheerful prophet, but we shall not all agree with his views.

The book is a really valuable one, and is carefully written and free from serious errors. In a future edition Rayner's papers on the formation of trimethylene glycol in crude glycerin ought to be noted.

H. E. Cox.

LES PLANTES À PARFUMS DES COLONIES FRANCAISES. Report by M. E. Maunier to the Congres du Comite National des Conseillers du Commerce Exterieur, Nice, Janvier, 1928. Pp. 134. Marseilles: Institut Colonial. 1928. Price, post free, France 10 fr., abroad 12 fr.

This address, which has been reprinted by the Institut Colonial de Marseille, gives details for each colony as to its present output of perfumery materials, and of its possibilities as regards soil and climate for their further development. It is claimed that the French colonies, comprising nearly 11,000,000 sq. kilometres, and having the most varied soil and climate, should be able to produce practically all the natural raw materials required by the perfumer, instead of France importing from foreign countries, as in 1926, more than 15,000 quintals of essential oils, valued at more than 153,000,000 francs.

W. H. SIMMONS.

Publications Received.

ASPECTS OF AGE, LIFE AND DISEASE. By SIR HUMPHREY ROLLESTON, M.D.
London: Kegan Paul, Trench, Trubner & Co., Ltd. 1928. Price 10s. 6d. net.

A collection of papers on subjects allied to medicine, including: Concerning old age—Some medical aspects of holidays—The medical aspect of tobacco—Professional careers—Poetry and physic—Medical aspects of Samuel Johnson, etc.

EXPERIMENTS WITH HANDWRITING. By ROBERT SAUDEK. Pp. 395. London: George Allen and Unwin Ltd. 1928. Price 10s. net.

The development of the graphic faculty—Relative speed of the act of writing—Authentic and spurious expression in handwriting—The central nervous system and the act of writing—Individual features of handwriting and their symptomatic significance.

ANNUAL SURVEY OF AMERICAN CHEMISTRY. Vol. III. Edited by CLARENCE J. WEST. New York: Chemical Catalog Co. 1928. Price \$3.00.

SIMPLE QUALITATIVE ANALYSIS. (Practical Chemistry, Part III.) E. J. HOLMYARD. London: G. Bell & Sons. Price 1s.
Elementary text-book.

QUALITATIVE ANALYSIS. By W. WARDLAW, D.Sc., and F. G. PINKARD, M.Sc. Pp. 166. London: Longmans, Green & Co. 1928. Price 3s. 6d.
Elementary text-book. Scheme of analysis used in laboratories of Birmingham University.

FOOD PRODUCTS. THEIR SOURCE, CHEMISTRY AND USE. By E. H. BAILEY and H. S. BAILEY. Pp. 563. Philadelphia: P. Blakiston's Son & Co. 1928.

HERMES OR THE FUTURE OF CHEMISTRY. By T. W. JONES. Pp. 88. London: Kegan Paul, Trench, Trubner & Co., Ltd. Price 2s. 6d. net.
A volume in the "To-day and To-morrow" Series.

ALKALINE ACCUMULATORS. By J. T. CRENNELL and F. M. LEA. Pp. 132. London: Longmans, Green & Co. 1928. Price 10s. 6d. net.

A HANDBOOK OF CLINICAL CHEMICAL PATHOLOGY. By F. SCOTT FOWWEATHER, M.D., M.Sc. Pp. 216. London: J. & A. Churchill. 1929. Price 8s. 6d.

THE STRUCTURE OF AN ORGANIC CRYSTAL. By SIR W. H. BRAGG, F.R.S. (Fison Memorial Lecture, 1928.) London: Longmans, Green & Co. Price 1s. 6d. net.

VOLUMETRIC GLASSWARE. By VERNEY STOTT. Pp. 232. London: Witherby. Price 20s. net.

CATALYTIC PROCESSES IN APPLIED CHEMISTRY. By T. P. HILDITCH, D.Sc., F.I.C. Pp. 360. London: Chapman & Hall. Price 16s. net.

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

AN Ordinary Meeting of the Society was held in the Chemical Society's Rooms, Burlington House, on Wednesday, February 6th, the President, Mr. Edward Hinks, being in the chair.

Certificates were read for the first time in favour of:—Frank Atkins, Edmund Baron Bennion, M.Sc., A.I.C., John Haslam, M.Sc., A.I.C., Stanley Gordon Kendrick, B.Sc., A.I.C., Bryn Jones, B.Sc., A.I.C., John Upton Lewin, B.Sc., A.I.C., Leslie John Walker.

Certificates were read for the second time in favour of:—William Bennett Adam, M.A., A.I.C., Alfred Louis Bacharach, B.A., F.I.C., Andrew Dargie, B.Sc., A.I.C., and Wadie J. Itayim.

The following were elected Members of the Society:—Edwin Herbert Bunce, A.I.C., Frederick O'Brien, M.Sc., F.I.C., William Macro Seaber, B.Sc., F.I.C., John Graham Sherratt, B.Sc., F.I.C.

The following papers were read and discussed:—"The Fatty Acids and Component Glycerides of some New Zealand Butters," by T. P. Hilditch, D.Sc., F.I.C., and Eveline E. Jones, M.Sc.; "A New Test for Boric Acid and Borates," by A. Scott Dodd, B.Sc., F.I.C., F.R.S.E.; and "The Determination of Beryllium in Rocks," by B. E. Dixon, M.Sc., A.I.C.

Obituary.

THOMAS PORTER BLUNT, M.A., F.I.C.

THE Society of Public Analysts has lost one of its oldest members by the death of Thomas Porter Blunt, who died quite suddenly in his sleep on February the 8th, in his 87th year.

He was born in Shrewsbury and educated at Friar's School, Bangor, and Magdalen College, Oxford, where he studied chemistry under the late Professor Harcourt, taking first class honours in Natural Science in 1864. From Oxford he returned to his native town, joining his father in his business as pharmacist.

With the passing of the Food and Drugs Act he was appointed Public Analyst for Shropshire, which post he retained for over fifty years, and on his retirement, three years ago, his services were retained as Consulting Analyst to the County. He also acted as Official Agricultural Analyst for Shropshire, and Public Analyst for the Counties of Montgomery and Merioneth, and for the Borough of Wenlock.

Up to within two years of his death he was actively engaged in his laboratory, but a serious accident when on holiday in North Wales prevented him carrying on with the work he loved so well, and I know that at the last "he was very tired after months of inactivity and discomfort." Apart from his Public Analyst's work, he was also Gas Examiner to the town of Shrewsbury until 1917, and he was on the Board of Examiners to the Pharmaceutical Society from 1886 to 1893.

Blunt joined the Society of Public Analysts in the year the Society was founded, 1874, and served on the Council in 1891-1892. He published the following papers in THE ANALYST:—"Permanganate Process for Water" (4, 94); "Effect of Light on some Reagents and Chemical Compounds" (5, 79); "Williams' Nitrogen Process" (6, 202); "Use of Platinic Chloride as an Indicator in Determination of Free Iodine" (7, 135); "Ferrocyanide Test for Zinc" (9, 232); "Determining the Fixed Acids in Butter and Margarine" (13, 110); "Notes on Tabarie's Process for the Indirect Determination of Alcohol" (16, 221); "Note on Ginger" (21, 309); "Note on the Separation of Arsenic" (48, 596); "The Analysis of Commercial Lime" (51, 625).

All Public Analysts have reason to be grateful for his elegant simplification of Tabarie's formula, for his neat method for determining nitrates in water, and for his very convincing article on the detection of "exhausted" ginger.

In 1865 he contributed an original paper on phosphide of magnesium to the Transactions of the Chemical Society, and other chemical contributions will be found in the *Chemical News* and the *Pharmaceutical Journal* during years 1880 to 1893.

His outstanding contribution to science was his work, in association with Sir Arthur Downes, on the action of light upon bacteria. As early as 1877 he proved definitely the bactericidal effect of sunlight, and this pioneer work, which was published in the Proceedings of the Royal Society, London (1877, XXVI, 488), laid the foundations for modern work on actinotherapy; and it is only with the

revived interest in "light" treatment that Blunt's work has received due recognition.

It was my good fortune to join Blunt in his analytical work in 1912; this was the beginning of an association which was marked by Blunt's unfailing willingness to share his knowledge and experience with a man many years his junior, and by a staunch friendship lasting until his death.

He had many interests apart from his work; a keen and able field botanist, he was a vice-president of the Caradoc and Severn Valley Field Club, acted as honorary curator of the botanical section of the Shrewsbury Museum, and as a judge of wild flowers at the Shrewsbury Show for half a century. An enthusiastic educationist, he served on the board of management for several schools.

A love of the Classics, formed in his Oxford days, was retained throughout his life, and his ability as a Latin and Greek scholar was of no mean order. In his younger days he was a rowing man, being in his College crew, and he also served as a volunteer.

Blunt combined exceptional charm of manner with a generous and kindly disposition; a scholar and a gentleman, he did much to establish the traditions and dignity of his profession, and his example is one which a younger generation of Public Analysts may well strive to emulate.

HAROLD LOWE.

JAMES WEST KNIGHTS.

WE have recently had to mourn the loss of several of the oldest members of our Society, and the death of James West Knights, at the age of 75, has now added another to the list.

James West Knights was the second son of Mr. James Knights, of St. Ives, Hunts. He was educated at St. Ives Grammar School and at Barton School, Wisbech. After leaving school he served an apprenticeship with a local druggist, and then came to London to undergo a course of training in analytical chemistry.

His professional career began by his becoming chief analyst to a firm of chemical manufacturers in Flint, and shortly afterwards, at the early age of 25, he was appointed Public Analyst for the Borough and County of Cambridge, the Isle of Ely, the County of Hunts., and the Boroughs of Wisbech and King's Lynn. These appointments he held until last year, when he retired, after 50 years' service. For many years he also acted as gas examiner to the Cambridge Corporation.

West Knights joined our Society in 1878, and he contributed several papers to the early volumes of *THE ANALYST*, including a method for the estimation of nitrates in water (1882, 6, 56) and a description of the familiar form of extraction apparatus which bears his name (1886, 8, 65).

For many years past he took no part in the work of the Society, and was therefore personally known to only a few of our members.

EDITOR.

The Determination of Small Amounts of Alcohol in the Human Subject.

By JOHN EVANS, F.I.C., AND A. O. JONES, M.A., F.I.C.

(Read at the Meeting, December 5, 1928.)

WHEN a person drinks alcohol some of it is absorbed as such into the blood, and as this blood passes through the kidneys a certain amount is excreted in the urine.

As early as 1915 Widmark published results of the examination of the urine of persons arrested for drunkenness, and since then the subject has been investigated by others. The object of this paper is to draw attention to an extensive series of investigations made at Sheffield University by Professor Mellanby and Dr. Southgate in 1924–1925, in order to obtain information as to the rate of absorption of alcohol into the blood and the rate of its excretion in the urine, and more particularly to draw attention to the ingenious apparatus employed by Dr. Southgate to determine small amounts of alcohol in blood and urine. The apparatus is so designed that only 2 c.c. of the sample are required for a single determination.

We have had considerable experience in the use of the apparatus, and find it easy to manipulate, and, judging by the agreement obtained between duplicate determinations, highly accurate. As it may be necessary at any time in forensic practice, or even in the Public Analyst's ordinary work, to determine alcohol in low concentrations, we think that this method ought to be more widely known.

SUMMARY OF THE PROCESS.—Two c.c. of urine are evaporated slowly at 80° C. in a current of air which has previously been washed by passing it through concentrated sulphuric acid.

The mixture of air and alcohol vapour is led through a mixture of 15 c.c. of *N*/5 potassium dichromate solution and 20 c.c. of concentrated sulphuric acid in an apparatus specially designed to promote efficient interaction. The alcohol is oxidised to acetic acid at the expense of some of the dichromate, in accordance with the equation— $\text{CH}_3\text{CH}_2\text{OH} + 2\text{O} = \text{CH}_3\text{COOH} + \text{H}_2\text{O}$.

The unreduced dichromate is determined by causing it to liberate iodine from potassium iodide and titrating the liberated iodine with *N*/10 sodium thiosulphate solution. The reduced dichromate is thus known by difference, and is calculated to its equivalent of alcohol.

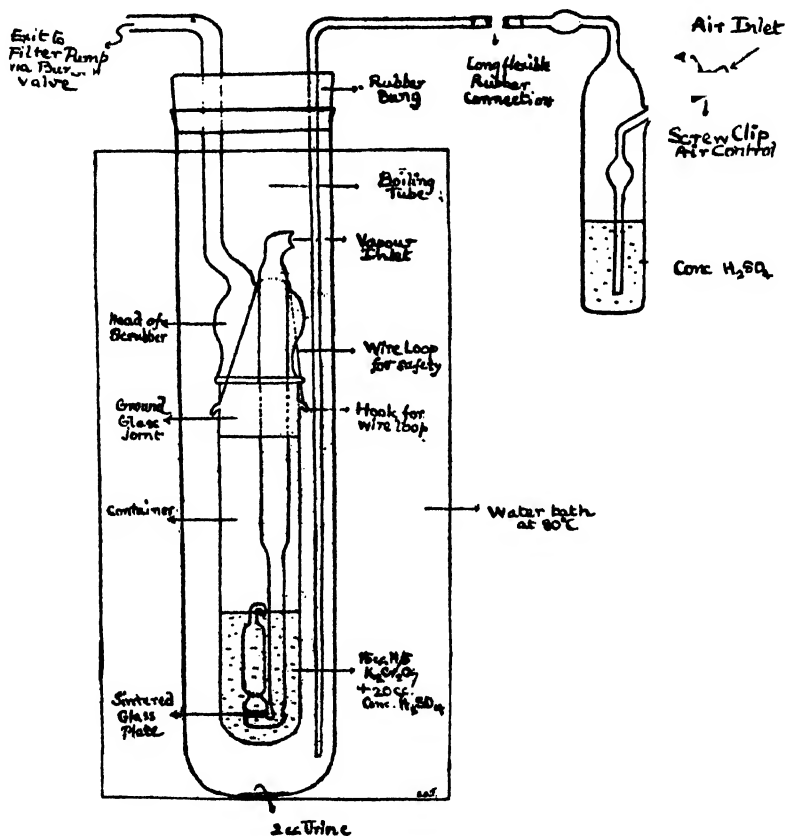
DESCRIPTION OF THE APPARATUS.—The apparatus is a modification, devised by Dr. Southgate, of an apparatus used by Canan and Sulzer, and consists of three parts: a boiling tube, a container, and a scrubber.

The large outer boiling tube is closed by a rubber bung pierced by two holes. Through one hole passes a narrow glass tube reaching nearly to the bottom of the

boiling tube. The inlet of this tube is connected with the sulphuric acid air-washer. Through the other hole passes the exit tube of the scrubber, which is connected with an ordinary filter pump.

Inside the boiling tube is the container, in which the acid dichromate solution is placed. By means of a ground-glass joint this container is fitted to a glass bulb-shaped head, which is in communication with the exit tube to the pump.

Fused into this glass head is a wide tube, the inlet of which is open to the interior of the boiling tube. At the other end of this tube, which reaches nearly



to the bottom of the container, is an ingenious scrubber, containing a sintered glass plate. The scrubber is immersed in the acid dichromate solution, and 2 c.c. of the urine to be examined are placed in the outer boiling tube. Fifteen c.c. of the $N/5$ dichromate solution are placed in the container, and 20 c.c. of concentrated sulphuric acid added, the container being kept cool in water. The container is then fitted to the scrubber head, wired on for safety, and by means of the rubber bung the boiling tube is attached. The narrow inlet tube is connected with the sulphuric acid air-washer, and the exit tube with the pump. When a steady aspiration is established the apparatus is weighted with a heavy weight and almost

completely immersed in a water-bath maintained at 80° C. The current of air draws the volatile products of evaporation of the urine through the dichromate solution, the sintered glass plate of the scrubber reducing the vapour to a stream of minute bubbles and thereby ensuring rapid and complete oxidation. When evaporation is complete (in 20–30 minutes) the apparatus is removed from the bath, the boiling tube disconnected, and the dichromate solution transferred to a litre flask.

The container and scrubber are washed several times with water by suction at the pump, and the combined liquids are diluted to about 500 c.c. About 1 gm. of solid potassium iodide is now added to the solution, and the liberated iodine is titrated with *N*/10 sodium thiosulphate solution, starch being used as an indicator. Factor: 1 c.c. of *N*/10 thiosulphate = 0.00115 gm. of alcohol.

Manipulation of the apparatus is easy, and with ordinary care accurate results are obtained. The following details and precautions readily suggest themselves to the operator.

A steady uni-directional flow of air is essential, and its rate of flow can be controlled by means of a screw-clip on a piece of pressure-tubing on the inlet to the air-washer. The mercury column of the pump should stand at 4–6 inches, and the evaporation of the 2 c.c. of urine should be complete in 20 to 30 minutes.

An obvious danger is a sudden reduction in the aspiration, which may cause alcohol vapour to be blown back into the air-washer and retained there. It is therefore advisable to interpose a Bunsen valve between the exit from the apparatus and the pump. A reversal of the air-current, due to failure of the pump, is thus avoided.

For the same reason a vigorous and steady aspiration should be established before the apparatus is placed in the water-bath; otherwise expansion of the air in the boiling-tube may drive alcohol vapour into the air-washer.

Full dilution of the dichromate solution is, of course, essential, and care must be taken that no undiluted liquid remains on the sides of the litre flask, as it is sufficiently acid to liberate iodine independently of the dichromate.

The urine should be tested for freedom from glucose, as the presence of a fermentable carbohydrate makes the interpretation of the results impossible, as some of the alcohol might be derived from the sugar.

It is our practice also to test for albumin.

PHYSIOLOGICAL RELATIONS.—The following information is extracted from a paper by Drs. H. W. Southgate and G. Carter, in the *British Medical Journal* (March 13th, 1926, pp. 463–469):—"The alcohol in the blood is related to the amount of alcohol consumed when this is imbibed under constant conditions, and the ratio between the alcohol in the blood and the alcohol in the urine is surprisingly constant and is of the order of 1.35.

The presence of alcohol in the blood is recognisable, even 12 hours after the time of drinking.

The concentration of alcohol in the blood attains a maximum value about $1\frac{1}{2}$ hours after consumption, and falls at the rate of about 12 mgrms. per hour per 100 grms. of blood.

If the same person consumes equal amounts of alcohol in widely different concentrations, it is found that the alcoholic concentration rises more rapidly, and to a higher point, in the case of the stronger solution. Also, the slower the rate of drinking, the lower will be the maximum concentration attained.

All foods tend to depress the absorption of alcohol from the stomach and intestines and thereby lower the alcoholic concentration of the blood, but some have such a potent action in depressing blood alcohol as to be almost specific. Among these foods bread and milk stand out pre-eminent. Food however makes little difference to the ratio between blood alcohol and urine alcohol.

It has been shown by Schwersheimer that if abstainers, moderate drinkers and heavy drinkers take the same quantity of alcohol when other conditions are equal, then the concentration of alcohol in the blood is highest in the case of the abstainer and lowest in the heavy drinkers. In other words, a kind of tolerance has been established in the case of the heavy drinker.

FACTORS.—If a sample of urine has been excreted when its alcohol content is at its maximum point (*i.e.* $1\frac{1}{2}$ hours after consumption), the following relations can be used to determine the amount of alcoholic liquor consumed:—

Whisky.—Ninety-six c.c. of absolute alcohol (=235 c.c. of whisky) correspond to 200 mgrms. of alcohol per 100 c.c. of urine.

Beer.—Ninety-six c.c. of absolute alcohol (=1920 c.c. of beer) correspond to 178 mgrms. of alcohol per 100 c.c. of urine.

i.e. for whisky:

Mgrms. of alcohol per 100 c.c. $\times 0.04137$ = fluid ounces consumed.

for beer:

Mgrms. of alcohol per 100 c.c. $\times 0.0190$ = pints consumed.

EXPERIMENTAL WORK.—In order to satisfy ourselves as to the working of the analytical process described, and to assure ourselves of the possibilities of the method as a chemical determination of the amount of alcoholic liquor consumed, we made the following experiments.

(1) *With a solution of pure alcohol.* A sample of *Spiritus Vini Rectificatus*, B.P., was taken, and its alcoholic content determined by specific gravity. An accurate 1 per cent. v/v solution was then made, and the alcohol in it determined by Dr. Southgate's method. The amount of alcohol found per 100 c.c. was 0.68 gm.

By calculation from the specific gravity 0.69 gm. of alcohol was present in 100 c.c.

(2) Two samples of urine were supplied by a person who stated that he had taken a quantity of beer at about 7 p.m.

The first sample of urine, excreted at 7.20 p.m., showed 27.3 mgrms. per 100 c.c.

The second sample of urine, excreted at 8.30 p.m., showed 55.5 mgrms. per 100 c.c.

Taking the figure found with the second sample, the consumption of beer works out to 1.05 pint. After the analysis the consumer stated that the quantity taken was one pint.

(3) Sixty c.c. (2.1 fl. ozs.) of whisky, diluted with 60 c.c. of water, were drunk rapidly on an empty stomach. The alcohol in the urine was then determined.

(i) 50 minutes after consumption, 23 mgrms. per 100 c.c.

(ii) $1\frac{1}{2}$ hours after consumption, 57 mgrms. per 100 c.c.

(iii) $2\frac{3}{4}$ hours after consumption, 17.5 mgrms. per 100 c.c.

The maximum figure obtained (57 mgrms. per 100 c.c.) corresponds to 2.3 fl. ozs. of whisky. The quantity drunk was 2.1 fl. ozs.

(4) Two samples of urine were provided by a person who had taken two pints of beer, followed by two small whiskies.

The first sample, excreted 45 minutes after consumption, showed 92.5 mgrms. per 100 c.c.

The second sample, $1\frac{1}{2}$ hours after consumption, showed 129 mgrms. per 100 c.c.

By calculation from the amount consumed, the maximum concentration of alcohol attained should be 150 mgrms. per 100 c.c.

The necessity for determining alcohol in the human subject, either during life or *post-mortem*, is one which can easily arise in forensic chemistry. The method described is admirably suited for this purpose, provided that no other volatile oxidisable matter is present.

In the present congested state of traffic in our cities the intoxicated motorist is a danger both to himself and to the public. How little alcohol is required to upset the higher mental faculties (which by a well-known physiological law are affected first) we are not in a position to state—the question is pre-eminently one for the physiologist, but our own experiments show that when a quantity of alcoholic liquor, insufficient to produce intoxication in the ordinary sense of the term, is consumed, the alcohol excreted in the urine can be determined.

We have had the opportunity of determining the alcohol content in numerous samples of urine taken from persons arrested for being drunk in charge of motor cars.

For comparison, therefore, we append a few of these results to indicate the degree of concentration of alcohol in the urine in cases where large amounts of alcoholic liquors have been consumed.

	1st Sample.		2nd Sample.		3rd Sample.	
	Time.	Alcohol per 100 c.c. Mgrms.	Time.	Alcohol per 100 c.c. Mgrms.	Time.	Alcohol per 100 c.c. Mgrms.
1.	9.15 p.m.	269	10 p.m.	261	11.15 p.m.	202
2.	1.0 a.m.	292	2 a.m.	264	—	—
3.	11.45 p.m.	336	1.10 a.m.	302	—	—
4.	8.50 p.m.	395	10.15 p.m.	373	—	—
5.	12.50 a.m.	412	—	—	—	—
6.	5.10 p.m.	268	5.55 p.m.	285	7.30 p.m.	211
7.	1.8 a.m.	342	2.48 a.m.	287	—	—
8.	4.40 p.m.	349	5.5 p.m.	355	—	—
9.	11.15 p.m.	286	12.20 a.m.	243	—	—
10.	4.15 p.m.	293	—	208	—	—
11.	9.0 p.m.	378	9.45 p.m.	338	—	—

In conclusion, we may quote a statement from a paper read by Dr. Godfrey Carter before the Society for the Study of Inebriety: "Two hundred mgrms. of alcohol per 100 c.c. of urine suggests moderate intoxication, 360 mgrms. per 100 c.c. of urine suggests definite drunkenness.

The apparatus (excluding the sulphuric acid air-washer) is supplied by: Messrs. The Scientific Glass Blowing Co., 12-14, Wright Street, Oxford Road, Manchester.

REFERENCES.

- Southgate, H. W. *Biochem. J.*, **19**, 737.
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DISCUSSION.

Sir WILLIAM WILLCOX congratulated the authors on their paper, and said that he thought the chemical tests outlined would ultimately come into general medico-legal use. At present the whole position was unsatisfactory, for in general legal practice it had not been decided what constituted drunkenness.

He then proceeded to read from the considered report of a committee appointed by the British Medical Association, which purported to give a definition of drunkenness, and which described the various physical and psychological tests to be applied to a suspected person.

The present state of the law, Sir William proceeded, was almost ludicrous. The definition evolved by the committee (of which he himself was a member) was worthless from the legal point of view, because the popular legal idea of drunkenness was a condition of disorderliness and complete helplessness due to the consumption of alcohol. There was nothing in the legal acts suggesting that a man was drunk when he had lost such higher faculties as an ability to play billiards or drive a motor car. The result was that there was a tendency not to regard a person as drunk unless he was "dead drunk."

He had been giving evidence, he said, a few days previously in an important case. The accused person had responded to all the tests outlined, but no single one of them could be said to be proof that he was drunk; drunkenness could only be diagnosed by a combination of all the tests, and even then, from a legal point of view, the diagnosis appeared to be insufficient.

The law was unsatisfactory in that, unlike arsenic or strychnine, drink could not usually be proved to be in the system in sufficient amount to cause drunkenness; and there was a tendency nowadays to give the benefit of the doubt to the accused person. The milder degrees of drunkenness were not recognised by the law, and for that reason the definition evolved by the B.M.A. committee was of no legal value.

Hence, Sir William continued, the present paper was of very great value in that it pointed the way to placing the diagnosis of drunkenness on a scientific basis. A good deal of work, however, had still to be done: the chemical data were so far insufficient. It was not yet possible to say what percentage of alcohol meant drunkenness and what sobriety. He would like to know, again, how the various psychological tests were affected by the presence of different quantities of alcohol in the blood and urine.

Another difficulty that occurred to him was the case of the "old toper." Did he get an excessive amount of alcohol in the blood, or had the body developed the power of oxidising and preventing absorption? There was also the legal difficulty that a man could not be forced to give evidence against himself by the provision of specimens of blood or urine from himself.

The one great advantage of the test at the moment was that it would prevent the conviction of innocent persons, for the absence of alcohol would disprove drunkenness. In this connection Sir William related the story of an unfortunate person suffering from a nervous disease who had walked some distance to the park, only to discover that he had no money in his pocket for his 'bus fare home. He walked rather unsteadily up to a policeman and asked him to lend him twopence—whereupon he was promptly arrested for being drunk.

Mr. E. R. BOLTON suggested that the paper should have been entitled "Chemical Tests for Drink," the object being to determine how much alcohol a man had taken. The acute question of the definition of drunkenness had become of importance in reference to motor drivers, though some men were more dangerous, even when sober, than a skilled driver who might have taken a little drink. The test, he contended, should be used for sorting-out purposes, to decide whether an accused person had, or had not, taken drink. Other points should, of course, be considered, and due regard should be paid to the fact that a man who had been shaken by an accident was not in a condition to be judged as to his competency to drive a car.

Dr. B. S. EVANS said that he had often tried to determine traces of chronic acid by the amount of iodine liberated from potassium iodide, but never with satisfactory results, and he had had to fall back on colorimetric determination.

Mr. J. R. NICHOLLS remarked that the apparatus was neat and efficient for the determination of volatile oxidisable matter. But the acidity of the oxidising mixture was so great, and the conditions of oxidation so drastic, that many other substances besides ethyl alcohol would be attacked, *e.g.* acetone. A comparatively small proportion of oxygen was necessary to oxidise ethyl alcohol to acetic acid, whereas most other substances being oxidised to carbon dioxide and water required much larger proportions. On the assumption that all the oxygen so used had produced acetic acid from ethyl alcohol, a very small quantity of impurity would show as a much larger quantity of alcohol. The test, therefore, could

only be of value as a negative test to indicate that a man had not taken alcohol ; a positive result would be liable to a highly dangerous interpretation.

Dr. ROCHE LYNCH said that the test had been proved to be sound some two years previously. The apparatus had been found to give accurate results when known quantities of alcohol were taken, and when acetone alone was present negative results had been obtained. In attempting to co-ordinate the amount of alcohol found, however, they were confronted with individual variation, time relations between the taking of the alcohol, the accident and the test, and the rate at which the alcohol was consumed. These, in his opinion, made the test difficult of interpretation, so far as court cases were concerned. Finally, samples of blood or urine could only be taken from a prisoner with his full consent.

Mr. J. EVANS replied that their idea was simply to bring the apparatus (which was made by the Scientific Glass-blowing Company, Manchester) before the Society. They were not responsible for the taking of the police samples, but had carried out the analyses on those handed to them. With regard to the legal aspect, he understood that it was not a legal offence to be drunk; a man had to be drunk and disorderly, or drunk in charge, or drunk and incapable. He did not wish to infer that the man who had taken a pint of beer was drunk. As regards interfering substances, there was always the case of the diabetic patient, and he intended to examine diabetic urine; but his business was not to interpret results: he tested for alcohol, albumin, and sugar and sent in his report. Tests made on non-alcoholic urines had given a blank every time. Not all the experiments had been referred to: the remainder would be published.

The Determination of Aluminium in Steel.*

BY A. T. ETHERIDGE, B.Sc., F.I.C., M.B.E.

ALUMINIUM is used as a deoxidiser for molten steel in the ladle, but usually only a trace remains in the metal. The effect of aluminium, below 0.2 per cent., is practically negligible (except in the form of inclusions of alumina which are very detrimental; this, if present, is not estimated here, as it is insoluble in acid, due to the high temperature to which it has been exposed). Steels with 0.5 per cent. and upwards have been investigated by Hadfield (*J. Iron and Steel Inst.*, 1890, 2, 161), and later by Guillet (*Revue de Métallurgie*, 1905, 312), but have not achieved commercial importance. Recently, however, a chromium steel with 1.2 per cent. of aluminium has come into prominence for the nitrogen process of surface-hardening (Guillet, *Compt. rend.*, 1928, 186, 1177).

The method of determining aluminium in steel, as given in technical books dealing with steel analysis, consists in precipitating it as phosphate from acetic acid solution, the iron being kept in the ferrous state by sodium thiosulphate. This has been tested by adding 0.01 and 0.02 per cent. of aluminium to electrolytic

* Communication from the Research Department, Woolwich.

iron. In the case of a 0.01 per cent. addition no precipitate was obtained, and with 0.02 per cent. addition the amount recovered was less than 0.01 per cent.

The method is therefore unreliable for small amounts of aluminium. As regards larger amounts, it has been shown by Clennell (*Mining Magazine*, May, 1922) that aluminium phosphate is of variable composition according to the amount of excess of reagent and conditions of precipitation.

Experiments were therefore made with a view to discovering a method which could be relied upon for all amounts of aluminium. Briefly stated, the iron is removed from a chloride solution by extraction with ether, and other interfering metals are removed by electrolysis over a mercury cathode from a sulphuric acid solution. The apparatus and the operations are the same as given by the author in a previous communication. (The Determination of Vanadium in Steel, *ANALYST*, 1928, 53, 423.)

The liquid, after electrolysis, contains the aluminium, together with manganese (and vanadium and titanium if present). The aluminium is precipitated with ammonia and, after weighing, is analysed to obtain the correction for other substances present, in order to arrive at the actual weight of aluminium oxide. The details are as follows: In the case of most steels the weight taken is 10 grms. But, if aluminium is known to be present as a constituent, and the amount is also approximately known, a weight is taken which will give about 0.1 gm. of oxide; on account of the gelatinous nature of the precipitate it is not advisable to handle much more than this. A weight of 10 grms. of steel is dissolved in 100 c.c. of concentrated hydrochloric acid (less for smaller weights), oxidised with the minimum amount of concentrated nitric acid, evaporated to a low volume, transferred to a separating funnel, and extracted with ether, as described in the paper referred to previously (*loc. cit.*).

The liquid is treated with sulphuric acid and electrolysed, the electrolyte removed and evaporated, traces of mercury precipitated with hydrogen sulphide, and the filtrate from the precipitate boiled down, as therein described. After the addition of 5 grms. of ammonium chloride the aluminium is precipitated with ammonia (sp. gr. 0.940), methyl red being used as indicator according to the instructions given by Blum (*Scientific Paper* 286, *Dept. of Commerce, U.S.A.*). The precipitate is filtered off on a filter paper of low ash, washed with weak ammonium chloride solution (Blum, *loc. cit.*), burnt in a low temperature muffle till the paper has been completely ashed, and ignited at 1200° C. for half an hour (Blum, *loc. cit.*). It is not necessary to make a double precipitation, unless the precipitate is considerable and the manganese is high in amount. A blank test must be made on the reagents by carrying through the process from beginning to end, omitting the steel, or, if preferred, using electrolytic iron. This usually gives a weight of about 1 mgrm. (This includes the alumina in the reagents, the filter paper ash, and traces of iron and silica from the reagents and glassware used after sulphating.)

The precipitate contains phosphorus pentoxide, ferric oxide, manganese oxide (very small), and chromic oxide (from a chrome steel). The phosphorus

pentoxide is derived from the steel, ferric oxide from reagents used after electrolysis, and manganese oxide (MnO) is usually negligible. The chromic oxide may be present in traces, as chromium is more difficult to remove by electrolysis than iron or nickel. If the weight of precipitate is not greater than 5 mgrms., it has been found that it is not worth while to analyse it, since, after the corrections have been made, the aluminium can be said to be not greater than 0.01 per cent. In such cases the aluminium should be estimated colorimetrically (see later). The precipitate is brought into solution by fusion with 1 grm. of potassium bisulphate (free from iron or containing only a known small amount) and extraction with water. If vanadium (or titanium) is known to be present, the vanadium pentoxide or titanium dioxide TiO_2 can be determined at once colorimetrically with hydrogen peroxide.

After the hydrogen peroxide has been boiled off the following oxides are determined on the same solution in the order given.

Ferric oxide is determined by nearly neutralising with ammonia, and adding sulphur dioxide solution, expelling the sulphur dioxide by boiling, cooling, and titrating with $N/100$ permanganate solution.

Manganese oxide is determined colorimetrically by the persulphate and silver nitrate method, allowance being made for the manganese already present from the previous operation.

Chromic oxide (if a chrome steel is being tested) is determined colorimetrically by oxidation with permanganate.

Phosphorus pentoxide. A weight of 0.1 grm. of electrolytic iron is dissolved in dilute nitric acid (sp. gr. 1.2), added to the liquid, and the iron (carrying all the phosphorus pentoxide) precipitated with ammonia (sp. gr. 0.940).

After filtering and washing, the precipitate is dissolved in 45 c.c. of dilute nitric acid (sp. gr. 1.2), poured while hot on to the paper. After the washing of the paper, the liquid is boiled down to 45 c.c., and 1.9 grms. of electrolytic iron dissolved in it. This process brings about the same conditions as are used for determination of phosphorus in steel, and the phosphorus is now determined alkalimetrically as usual.

This analysis gives all the information required to obtain the net weight of alumina in the precipitate. It will be seen from the table given below, that the phosphorus pentoxide forms the largest part of the correction to be made. If the result shows that the amount of aluminium is of the order of 0.01 per cent. or less, it will probably be sufficient to report the analysis in this way. If, however, more precise information is required, it is necessary to carry out a colorimetric analysis. The analysis is started again and carried out in the same way as far as the electrolysis stage. The washing liquid is hot water slightly acidified with sulphuric acid, instead of ammonium sulphate solution, as this has been found to interfere somewhat with the development of the correct shade of colour. The liquid is evaporated and traces of mercury removed as described. The filtrate is boiled down, cooled, and made up to 500 c.c.

An aliquot volume of 50 c.c. is first tested colorimetrically in order to decide on the best volume to take. The reagent used is aurin-tricarboxylic acid, and the process is used as described by Lundell and Knowles (*J. Ind. Eng. Chem.*, 1926, 60). The optimum amount of aluminium is 0.1 mgrm. and the range for suitable comparison with the standard solution is 0.05 mgrm. to 0.5 mgrm. A blank test must, of course, be carried out on all the reagents used.

TABLE OF RESULTS.

Steel. (10 grms.).	Weight of precipitate. Mgrms.	Corrections Mgrms.					Net weight of precipitate. Mgrms.	Gravimetric Analysis.		
		Fe ₂ O ₃ .	MnO.	P ₂ O ₅ .	Cr ₂ O ₃ .	Blank.		Aluminium.		
		Mgrms.	Mgrms.	Mgrms.	Mgrms.	Mgrms.		Found,	corrected for Al in steel	Added
								Total Per Cent.	used. Per Cent.	Per Cent.
Plain steel	4.8	0.8	<0.1	1.0	—	1.0	2.0	0.01	—	—
Same steel ..	11.0	0.8	0.1	3.0	—	1.0	6.1	0.03	0.02	0.02
Same steel ..	48.4	1.4	0.1	3.5	—	1.0	42.4	0.22	0.21	0.20
Nickel chrome steel with high phosphorus	9.6	1.4	0.1	3.5	1.2	1.0	2.4	0.01	—	—
Same steel ..	12.5	0.5	<0.1	5.2	0.5	1.0	5.3	0.03	0.02	0.02

COLORIMETRIC ANALYSIS.—The following example may be cited as typical of several:

Electrolytic iron 10 grms.

1/5 liquid=0.8 c.c. of standard solution (1 c.c.=0.1 mgrm. Al.)=4.0 c.c. for the whole liquid.

The same with 0.005 per cent. of aluminium added.

1/10 liquid=0.9 c.c. of standard solution=9.0 c.c. for the whole liquid.

Difference=5.0 c.c.=0.005 per cent.

The reagents alone, with 1/5 of the liquid required 0.5 c.c. of standard solution (which apparently indicates a trace of aluminium in the electrolytic iron used).

In testing a steel with these reagents, a correction of 0.0025 per cent. would be made.

The Determination of Small Quantities of Mercury in the Presence of Organic and Inorganic Compounds.

By R. ROBINSON.

THE determination of small quantities of mercury has been the subject of research by chemists during the past 20 years. The vast majority of these methods are applicable where mercury only is present, in which case no great difficulty arises except in the case of less than 0.002 g_m.

The high volatility of mercury and its salts is the cause of low results due to losses in the various operations necessary in obtaining the mercury free from metals of the hydrogen sulphide, ammonium sulphide and ammonia groups.

The method described in this paper, although not universally applicable, may, with slight modification, be used in most cases, and requires no elaborate apparatus.

For various researches it was necessary to determine between 0.002 and 0.040 g_m. of mercury in the presence of organic matter; the material having approximately the following composition:

Mercury	0.002-0.040 g _m .
Copper	0.010-0.200 "
Iron	0.100-0.250 "
Zinc	0.050-0.080 "
Calcium	0.060-0.100 "
Sodium chloride	0.100 "
Organic matter	0.300 "

The organic matter consisted of resinous bodies, and the mercury was present as a mixture of metallic mercury, mercuric oxide and an organic compound of mercury.

The method of removing the mercury with copper and determining it by volatilisation was found to be unsatisfactory; this can be understood from the paper by Gordon (*ANALYST*, 1920, 45, 41), who shows that, above 0.0100 g_m., the mercury is not precipitated quantitatively, and does not adhere well unless very large copper coils are used.

The later method of Evans and Clarke (*ANALYST*, 1926, 51, 224) by filtration through copper filings was not tried, this method not having been published before a satisfactory method had been found.

Colorimetric methods necessitated the separation of the copper, iron and zinc, with consequent losses of mercury, and with regard to these it might be mentioned that the diphenylcarbazide method of Menière (*Compt. rend.*, 1908, 754) was very unsatisfactory, the colour being considerably altered by a slight change in acidity.

The iodimetric method of Rupp is good for small quantities, but cannot be used in the presence of copper and iron. This also applies to a similar method proposed by Adanti which was, however, tried with pure mercury, standard solutions of one-tenth the strength suggested by him being used. The end-point is not sharp unless excess of sodium thiosulphate is added and the solution back titrated with $N/100$ iodine. This gives excellent results with quantities of 0.005 to 0.010 gm. of mercury, but only if the filtration of the mercury is carried out with the aid of the suction pump and a paper pulp pad, since it was found impossible totally to retain 0.005 gm. of mercury on an ordinary filter, owing to the fine state of division of the precipitate.

By precipitating the mercury with hypophosphorous acid, filtering on a pulp filter, and titrating with $N/100$ iodine and $N/100$ sodium thiosulphate satisfactory results are obtained with large and small quantities of mercury.

Some experimental results are shown, together with factors which influence the determination.

Howard (*J. Soc. Chem. Ind.*, 1904, 23, 151) has determined mercury by precipitation with hypophosphorous acid and weighing. The results were fairly satisfactory, although always slightly low, due to loss by volatilisation. To minimise the error, Howard used only large quantities.

Moser and Neissner (*Z. anal. Chem.*, 1928, 200), using a modification of Howard's method, obtained very satisfactory results by filtering on a counter-poised filter paper.

They also investigated the effect of impurities, and found that iron, lead, cadmium and zinc do not interfere, whilst copper rendered the method useless. As will be shown later, mercury can be determined in the presence of copper by means of hypophosphorous acid, if sodium chloride is added to the solution before precipitation.

The solutions required are:—(1) Hypophosphorous acid of sp. gr. 1.137; (2) $N/100$ iodine solution; (3) $N/100$ sodium thiosulphate solution.

A. PURE MERCURY.—The determination is carried out in a 350 c.c. conical flask provided with a glass cover. The solution containing the mercury is diluted to 200 c.c. with distilled water, and the acidity adjusted with hydrochloric acid, so that the solution contains 5 c.c. of 2*N* hydrochloric acid in excess; 2 grms. of sodium chloride and 0.010 gm. of paper pulp are added. Thirty c.c. of hypophosphorous acid (sp. gr. 1.137) are added, and the solution allowed to stand overnight.

The flask and contents are next heated on a water bath for 15 minutes and allowed to stand for 20 minutes, after which the liquid is filtered by suction through a well-packed paper pulp filter, and the flask and filter washed with cold distilled water. Thorough washing of both the flask and filter is essential to ensure the complete removal of all the hypophosphorous acid. The pulp and mercury are transferred to the original flask, the sides of the funnel being wiped with a piece of wet filter paper to remove adhering particles of mercury. This is also transferred

to the original flask, and 100 c.c. of distilled water and 2 c.c. of 30 per cent. acetic acid are added, followed by excess of $N/100$ iodine (at least twice as much as is required to combine with the mercury) and 2 grms. of potassium iodide. The flask is allowed to stand for at least 30 minutes, with occasional shaking, then treated with $N/100$ sodium thiosulphate solution in excess (1 c.c. excess is sufficient) and titrated to faint blue with $N/100$ iodine, starch being used as indicator (1 c.c. of $N/100$ iodine = 0.0010 gm. of mercury). A blank determination should be made, and the amount deducted from the result. This is due to the excess of iodine used, and to a small amount reacting with the pulp; it generally amounts to 0.0002 gm.

The paper pulp is prepared by digesting filter paper with 17 per cent. hydrochloric acid, filtering, and washing free from acid on a Buchner funnel.

The addition of a small quantity of paper pulp has the effect of causing the mercury to precipitate on its surface, thereby keeping it in a fine state of division and rendering the reaction of the iodine more rapid. This is a great advantage when using $N/100$ solutions.

RESULTS WITH MERCURIC CHLORIDE SOLUTION.—(1 c.c. = 0.002 gm. of mercury) no other metal being present. Above method used.

Solution. c.c.	Mercury present. Grm.	Mercury found. Grm.	Error. Mgrm.
1.	0.002	0.0018	0.2
3.	0.006	0.0058	0.2
5.	0.010	0.00975	0.25
5.	0.010	0.00964	0.36
5.	0.010	0.00964	0.36
5.	0.010	0.00994	0.06
5.	0.010	0.00975	0.25
5.	0.010	0.00970	0.30
10.	0.020	0.0197	0.30
15.	0.030	0.0295	0.50
15.	0.030	0.0295	0.50

The results are slightly low, averaging about 0.3 mgrm. This, no doubt, is due to the volatility of the mercury, as is shown later.

Effect of Acid.—The method described above was used, with excess of hydrochloric acid. The following results were obtained:

Excess of hydrochloric acid. c.c.	Mercury found. Grm.	Mercury present. Grm.	Error. Mgrm.
1 (2N)	0.00975	{ 0.010	0.25
5 "	0.00970		0.30
10 "	0.00955		0.45
5 (conc.)	0.0079		2.10

Excess of hydrochloric acid thus causes low results, and 5 c.c. of 2 N hydrochloric acid should be the maximum present. In this respect the figures disagree with

those obtained by Moser and Neissner (*loc. cit.*), who do not get low results when using 8–10 c.c. of concentrated hydrochloric acid in a volume of 150 c.c.

Effect of Volume of Liquid.—In these experiments 5 c.c. excess of 2 *N* acid were added in each case.

Volume. c.c.	Mercury found. Grm.	Mercury present. Grm.	Error. Mgrm.
25	0.00945	0.010	0.55
100	0.00965	0.010	0.35
200	0.00975	0.010	0.25

The mercury is not totally precipitated in a small volume with the usual excess of acid; this, no doubt, is mainly due to the increased concentration of hydrochloric acid.

Effect of Heating on Water Bath for Varying Times.—This is important on account of the volatility of mercury. It is essential that the liquid should be warmed to 80° C., otherwise there is a danger of the mercurous chloride not being totally reduced to mercury; on the other hand, there is a danger of losses due to volatilisation. With the type of water bath used throughout these experiments the liquid rose to its maximum temperature of 85° C. after 10 minutes.

Time of Heating on Water Bath.—The following results were obtained:

Minutes.	Mercury present. Grm.	Mercury found. Grm.	Error. Mgrm.
15	0.010	0.00975	0.25
30	0.010	0.00960	0.40
45	0.010	0.00935	0.65
80	0.010	0.00890	1.10

It is obvious from these analyses that the low results are due to the volatility of the mercury; consequently, every care should be taken to minimise them as far as possible.

The fact that, in general, the results are about 0.3 mgrm. low is probably due to the air space in the flask becoming saturated with mercury vapour, which is lost when filtering. The air space in the flask would generally be 100–150 c.c. The table below, calculated from the vapour pressure, shows the weight of mercury which would be present in 100 c.c. of air at various temperatures and a pressure of 760 mm.

Temperature. ° C.	Mercury per 100 c.c. Grm.
100	0.00032
90	0.00019
80	0.00011
70	0.00006
60	0.00003

With prolonged heating on a water bath a considerable volume of gases would escape, taking with it mercury in the form of vapour.

Effect of standing after Heating on Water Bath before Filtering.—The results obtained were as follows:—

Time of standing. Minutes.	Mercury present. Grm.	Mercury found. Grm.	Error. Mgrm.
0	0.010	0.0097	0.3
30	0.010	0.0098	0.2
60	0.010	0.0098	0.2

It has been suggested that very finely divided mercury oxidises on exposure to air. If this were the case, a low result should have been found. Since oxidation did not take place, it is not essential to titrate at once.

Effect of Quantity of Hypophosphorous Acid.—With only pure mercury salts present in the solution it makes no difference whether 5 c.c. or 40 c.c. of hypophosphorous acid are used. In the presence of copper, iron and other reducible compounds it is essential to use a large excess, partly on account of the loss of hypophosphorous acid due to oxidation, but mainly because mercury is not completely precipitated in the presence of these impurities unless a large excess of precipitant is used.

In the presence of impurities previously mentioned the results are usually 0.5 mgrm. too low, unless at least 30 c.c. of hypophosphorous acid are used.

B. DETERMINATION OF MERCURY IN THE PRESENCE OF IMPURITIES.—The effect of various impurities is shown in the following table:—

Mercury present. Grm.	Impurity. Grm.	Mercury found. Grm.	Error. Mgrm.
0.010	1 of KNO_3	0.0098	0.2
0.010	1.3 of $\text{Al}_2(\text{SO}_4)_3$	0.0097	0.3
0.010	1.0 of NaCl	0.00985	0.15
0.010	0.5 of Zn	0.00975	0.25

In the case of aluminium compounds it is essential to have sufficient excess of hydrochloric acid to prevent the precipitation of aluminium hydroxide or phosphate on heating. In one case a high result was obtained. This was due to the precipitation of aluminium hydroxide or phosphate which could be seen, and it rendered the solution extremely difficult to filter.

Iron.—Iron causes low results unless sodium chloride is present. Probably the iron prevents the complete precipitation of mercury, since if ferrous hydroxide or ferrous phosphates were present in the precipitate, a high result could be expected.

Mercury. Grm.	Iron. Grm.	Sodium chloride. Grm.	Mercury found. Grm.	Error. Mgrm.
0.010	0.50	—	0.0091	0.9
0.010	0.50	—	0.0089	1.1
0.020	0.50	—	0.0164	3.6
0.010	0.50	1	0.00975	0.25
0.010	0.50	1	0.00980	0.20
0.020	0.50	1	0.01960	0.40

Copper.—Copper in neutral or very faintly acid solutions gives a precipitate of copper hydride on the addition of hypophosphorous acid. Copper hydride decomposes slowly at ordinary temperatures and rapidly above 40° C., giving metallic copper and hydrogen.

Moser and Neissner endeavoured to determine copper by precipitation with hypophosphorous acid, but were unsuccessful. With hypophosphorous acid in the presence of excess of free hydrochloric acid no copper hydride or metallic copper is formed, but cuprous chloride is formed. This is filtered off with the mercury, and, reacting with the iodine and potassium iodide, gives erroneous results.

The addition of sodium chloride not only keeps the cuprous salts in solution, but also assists in the complete precipitation of mercury.

Mercury. Grm.	Copper. Grm.	Sodium chloride. Grms.	Mercury found. Grm.	Error. Mgrms.
0.010	0.5	—	0.0079	2.1
0.010	0.5	—	0.0143	4.3*
0.010	0.5	1	0.0097	0.3
0.010	0.5	2	0.0098	0.2
0.020	0.5	1	0.0195	0.4

* Brownish precipitate with hypophosphorous acid.

By keeping the solution sufficiently acid and adding sodium chloride, copper does not affect the result unless too small an excess of hypophosphorous acid has been added, in which case the whole of the mercury is not precipitated, and the mercury found is approximately 1.0 mgrm. less than that present.

DETERMINATION OF MERCURY IN THE PRESENCE OF COPPER, IRON AND ZINC.

	Copper. Grm.	Iron. Grm.	Excess 2N HCl. c.c.	Zinc. Grm.	Sodium chloride. Grm.	Hypo- phosphorous acid used. c.c.	Mercury present. Grm.	Mercury found. Grm.	Error. Mgrm.
1.	0.1	0.05	5	0.03	—	5	0.01	0.0092	0.8
2.	0.1	0.05	15	0.03	—	5	0.01	0.0086	1.4
3.	0.1	0.05	5	0.03	1	5	0.01	0.00875	1.25
4.	0.1	0.05	5	0.03	—	5	0.01	0.0079	2.10
5.	0.1	0.05	3	0.03	0.1	5	0.01	0.0091	0.90
6.	0.1	0.05	3	0.03	—	10	0.01	0.0089	1.10
7.	0.1	0.05	3	0.03	0.1	15	0.01	0.0096	0.40
8.	0.1	0.05	3	0.03	0.1	5	0.03	0.0269	3.10
9.	0.1	0.05	2	0.03	2	30	0.01	0.0098	0.20
10.	Impurities and treatment as No. 9 (average of 10 determinations)						0.01	0.00981	0.19
11.	0.1	0.05	2	0.03	1	30	0.02	0.0195	0.50
12.	0.1	0.05	2	0.03	1	30	0.02	0.0198	0.20
13.	0.04	0.05	3	—	2	30	0.01	0.0098	0.20
14.	0.08	0.11	3	—	2	30	0.01	0.0097	0.30
15.	0.12	0.17	3	—	2	30	0.01	0.0097	0.30

In the presence of sodium chloride and by using 30 c.c. of hypophosphorous acid the results show excellent agreement. With smaller quantities of precipitant and in the absence of sodium chloride, mercury is not completely precipitated if copper and iron are present. Once again the necessity for keeping the concentration of hydrochloric acid as low as possible will be noticed.

An attempt was made to separate the mercury and copper from the zinc, iron, etc., by precipitation with hydrogen sulphide, and subsequent solution in acid, followed by neutralisation with hydrochloric acid, before precipitating the mercury with hypophosphorous acid in the presence of copper only. This method always gave low results, which were due to the volatilisation of the mercury when dissolving in *aqua regia* or hydrochloric acid and bromine. At the same time, owing to the sulphur deposited by the interaction of the ferric iron and hydrogen sulphide, extreme difficulty was found in completely dissolving the copper and mercury sulphides, which were occluded by the sulphur.

C. DETERMINATION OF MERCURY IN THE PRESENCE OF ORGANIC COMPOUNDS.

—The destruction of the organic matter presents no great difficulty, since sodium and potassium nitrates do not affect the result. Consequently, heating in a sealed tube at 180° C. with fuming nitric acid is quite satisfactory in the majority of cases.

For the purpose for which this method was to be used it would have been fatal if the tube had burst, as, owing to the small quantities available, one burst tube would have spoilt the whole series. Consequently, it was decided to try other methods in which this danger was not present. Heating with sulphuric acid until the organic matter was destroyed in an ordinary Kjeldahl flask gave results which were 1 to 2 mgrms. low, and in the presence of small quantities of chlorides no satisfactory figures could be obtained, owing to the mercury volatilising.

It was found that by connecting the top of the Kjeldahl flask with two washing bottles and occasionally adding a crystal of potassium nitrate, the organic matter could be destroyed in a few hours at 150° C. With these precautions no mercury was lost, even in the presence of chlorides.

In this series the percentage composition of the impurities was always the same, but the amounts of the total impurities and the total mercury were varied.

The impurities present had the following composition:—Copper oxide, 27·7; iron oxide, 22·2; zinc oxide, 3·5; aluminium oxide, 2·1; silica, 2·8; and organic matter, 41·7 per cent.

Method.—The following was the method used:—From 0·2 to 0·5 grm. was placed in a Kjeldahl flask connected with two washing bottles, and heated in a liquid paraffin bath at 130°–150° C. with 10 c.c. of concentrated sulphuric acid, with the occasional addition of a crystal of potassium nitrate.*

When the organic matter has been completely destroyed and the solution no longer smells of sulphur dioxide, the contents of the washing bottles are added to the main bulk, the insoluble matter filtered off, and the filtrate neutralised with

* From 1 to 5 c.c. of nitric acid have also been used, with satisfactory results and shortening of time for the destruction of the organic matter.

sodium hydroxide, the temperature being kept below 50° C. The liquid is then rendered just acid with hydrochloric acid and 3 c.c. of 2*N* acid in excess are added, after which 2 grms. of sodium chloride and a trace of paper pulp (approx. 0.01 gm.) are added, the liquid diluted to 200 c.c., cooled, treated with 30 c.c. of hypophosphorous acid, and allowed to stand overnight. The method as previously outlined is then continued.

A blank determination should be made; this generally amounts to 0.0002 gm., being due to the excess of iodine necessary to give the blue coloration in the presence of the paper pulp.

The following table gives results thus obtained:

Impurity. Grm.	Mercury present. Grm.	Mercury found. Grm.	Error. Mgrm.
0.2	0.0100	0.0098 (average of 7 determinations)	0.2
0.5	0.0095	0.0094 " " 3 "	0.1
0.5	0.0024	0.0019 " " 2 "	0.5
0.5	0.0047	0.0044 " " 2 "	0.3
0.5	0.0142	0.0141	0.1
0.5	0.0190	0.0191	0.1
0.5	0.0250	0.0253	0.3

SUMMARY.—(1) Mercury can be determined in the presence of various impurities, notably copper, iron, zinc, sodium, and potassium, by precipitation with hypophosphorous acid and determination of the mercury by means of standard iodine.

(2) The results are generally 0.3 mgrm. too low, this being due to volatilisation of mercury. By adhering closely to the details of the method this loss will be constant.

(3) The effects of various factors influencing the estimation are shown.

(4) The volatility of mercury is proved to be a cause of low results.

(5) A method for the determination of mercury in the presence of organic matter is given.

In conclusion, the author wishes to thank Dr. P. E. Bowles, F.I.C., and Mr. R. Gill, M.Sc., for their assistance and advice.

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Erratum: The Fatty Acids and Component Glycerides of Some New Zealand Butters:—In the table on p. 80, line 26 (Feb. issue), for "Iodine value of solid fatty acids, 101.5" read "10.15."

Notes.

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

POISONING BY BITTERSWEET (*SOLANUM DULCAMARA*).

THE recorded cases of poisoning by bittersweet are few (*Vet. Record*, 1906, and *Farmer and Stockbreeder*, 1911), so that quite often doubt is expressed as to whether this plant is poisonous or not. The toxic principle is solanine, the berries containing some 0.5 per cent. of the alkaloid. Solanine is readily hydrolysed by mineral acids into solanidine, so that both alkaloids are found after the usual alkaloidal extraction methods have been used.

In cases of suspected poisoning I have found the usual Stas-Otto method of extracting alkaloids from viscera to be satisfactory, but as solanine is practically insoluble in ether and chloroform, a final extraction with warm amyl alcohol from ammoniacal solution is necessary, this being the most satisfactory solvent.

Solanidine is stated to be extracted from acid solution by ether, but I have not been able to verify this, my experience being that a mixture of solanine and solanidine is left after evaporation of the amyl alcohol extract.

The most useful tests on the mixed alkaloids were found to be:

(1) A concentrated solution of the alkaloids in amyl alcohol sets to a jelly-like consistence. (2) Phosphomolybdic acid gives a cream-coloured precipitate. (3) Fröhde's reagent gives a violet colour. (4) Nitric acid gives a purple colour on warming. (5) Vanadic sulphuric acid gives a red colour. (6) Ethyl sulphuric acid gives a red colour. (7) Concentrated sulphuric acid with bromine water gives red colours, forming in streaks. (8) Selenic sulphuric acid gives a red colour. (9) The haemolytic action on blood.

During the last few years I have had two definite cases of poisoning by bittersweet.

The first case occurred in the month of October, when a valuable foal was allowed into a field in which was a pond surrounded by masses of bittersweet. It was noticed that the foal ate the plant, but it was believed by those in charge of the animal to be harmless. When the foal became ill a veterinary surgeon was called in; he suspected poisoning, and when the foal died believed it might be due to deadly nightshade.

An examination of the stomach contents was made; the contents, on washing with water, were found to be in a very finely divided state, and no leaves or other characteristic parts of plants could be identified. Two hundred and fifty grms. of stomach contents were extracted for alkaloids, and 0.085 grm. of a mixture of solanine and solanidine was found.

In the second case, which occurred in the month of September, several cows died; and others were ill but subsequently recovered.

In this case the stomach contents consisted mainly of portions of leaves and fibrous stems which closely resembled those of bittersweet; no berries or seeds were found.

One hundred grms. of stomach contents yielded 0.06 grm. of mixed solanine and solanidine. The dung from other cows suffering, apparently, from the same

form of poisoning, was extracted for alkaloids, but nothing was found, so that it appears that solanine is not excreted as such in the dung.

A subsequent inspection of the field in which the cows had grazed revealed the fact that bittersweet was growing abundantly on the sides of a ditch.

In this case a veterinary examination and the *post-mortem* appearances suggested the possibility of solanine poisoning.

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THE EXTRACTIVES OF BRANDY.

IN *Aids to the Analysis of Food and Drugs*, Fourth Edition, (1918), p. 185, there occurs the statement that the total solids of brandy are "about 1 per cent." This statement had been carried on from the second edition (1899), at any rate, and through the third (1909). Whether it occurred in the first edition (1895), I do not know.

This figure of 1 per cent. was certainly a fair average up to 1910; from then until 1925 I have no adequate data for criticism, but since 1925 it certainly seems to be too high.

In twenty-six brandies I have analysed during the past three years the maximum figure has been 0.71 per cent. (weight/volume). For the purposes of this "Note" I have ventured on a rough classification into three groups:

No. 1 Group: The best-known brands, Three Star in each case, examined for the purposes of comparison. These consisted of Martell (two bottles), Hennessy, Otard, and Courvoisier.

No. 2 Group: Brandies supplied loose to Inspectors under the Sale of Food and Drugs Acts, which contained over 0.25 per cent. of total solids.

No. 3 Group: Brandies supplied loose to Inspectors under the Sale of Food and Drugs Acts, which contained up to 0.25 per cent. of total solids.

Actual figures (w/v) were as follows:

No. 1 Group: 0.61, 0.64, 0.56, 0.71, and 0.55 per cent.

No. 2 Group: 0.36, 0.38, 0.39, 0.55, 0.56, 0.62, and 0.62 per cent.

No. 3 Group: 0.07, 0.13, 0.14, 0.14, 0.15, 0.15, 0.15, 0.16, 0.17, 0.20, 0.20, 0.21, 0.21, and 0.25 per cent.

Excluding, for the time being, No. 1 Group, the principal cause of a drop in the total solids appears to be the change in public taste from a dark brandy to a pale brandy.

Apparently in the old days the demand for brown brandy arose from the knowledge that the article was colourless to commence with and steadily gained colour from the years it spent in the cask. Then came the period when the brown colour ceased to be any criterion of age, because burnt sugar was admittedly used to deepen the tint. This addition seems to have been taken as a matter of course. Thus Alexander and Meredith Wynter Blyth, in *Foods: Their Composition and Analysis* (Sixth Edition, 1909), p. 386, gave, as constituents of a typical brandy made from wine, 0.82 per cent. of sucrose and 0.37 per cent. of inverted sugar.

Brandy did not find a place in the *British Pharmacopoeia*, 1864, but appeared in the 1867 edition, with the description of having "a light sherry colour derived from the cask in which it has been kept" under the well-known title of *Spiritus*

Vini Gallici. Brandy continued to be an "official" substance in the 1885 and 1898 editions, with no recognition of caramel as a legitimate addition; but it disappeared in the avalanche of alterations that characterised the appearance of the 1914 edition. No figure was ever suggested for total solids. While the text of this "Note" is based on the falling-off in residue, it is of passing interest to observe that the Pharmacopoeia of the United States, where they have decennial revision, did not allow more than 0.5 grm. of residue from 100 c.c., in the 1905 edition. But the U.S.P., 1926, includes the following test:—When 20 c.c. are evaporated and dried "the weight of the residue does not exceed 0.30 grm." This is 1.5 per cent. for a maximum. Perhaps the former 0.5 per cent. was a misprint for 1.5 per cent.; the former would certainly, at any period in the analysis of brandy have condemned every reliable brand. In digression, it does not seem likely that the new name for brandy in the U.S.P., which is *Spiritus Vini Vitis* (*Sp. Vin. Vit.* being the prescribed short title), has anything to do with the matter, although in old days some high figures for total solids were found in brandies from sources other than French.

Squire's Companion, 19th Ed., 1916, appears to have got closest to the truth with the line: "The extractive matter varies from 0.6 to 1.5 p.c., and averages 0.75 p.c. w/v.," but to be on the high side then.

A most pleasant feature of the matter is the discovery that two of the most famous brands have never changed in their total solid content. *Lancet* analyses of one in 1899 and 1908 showed 0.69 and 0.67 per cent., my 1928 figures being 0.61 and 0.64. A 1905 analysis of another showed 0.69, the 1928 one being 0.56 per cent. It would appear that the best-known brands are to be relied on even in such an unimportant constituent as the total solids, which presumably means using the same type of oak cask for storage.

WILLIAM PARTRIDGE.

Notes from the Reports of Public Analysts.

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM.

REPORT OF THE CITY ANALYST FOR THE FOURTH QUARTER, 1928.

DURING the quarter 1333 samples were examined, of which 1177 were taken under the Sale of Food and Drugs Acts. Of these, 1085 were bought informally (27 adulterated), and 92 were formal samples (14 adulterated).

PRESERVED SAUSAGE.—Six samples were bought from shops in which notices were exhibited, such as, "All sausages exposed or offered for sale in this shop contain preservative," or "These sausages contain preservative," but in two cases the preserved sausage contained neither boric acid nor sulphur dioxide. Probably the shopkeeper had put up the notice believing he was selling preserved sausage, but the manufacturer, on that occasion, at any rate, had supplied sausage free from preservative.

It would appear to be much better if the Regulations had not allowed notices to be exhibited, but had required a declaratory label with each sample of sausage sold. The manufacturer who packs the sausage is in a position to know whether the article contains preservative, though the shopkeeper may not, and it would be quite easy to supply a preservative label with each retail sale.

OXYMEL OF SQUILL.—Twelve samples were of satisfactory composition, but one had been prepared with glucose syrup instead of honey. It was labelled "Oxymel Scillae," with the name of the vendors underneath, but no indication was given on the label that it was not of B.P. strength.

TALC IN DRUG TABLETS.—Seven samples each of potassium chlorate and phenacetin, and one each of calcium lactate, aspirin, and salol were examined. In each case the amount of drug present approximated to that stated, but there was considerable variations in the amounts of talc used in making the tablets. Of the 17 tablets, nine contained 0 to 0.4 per cent., three 1.4 to 1.7 per cent, three 2.8 to 2.9 per cent., and two, 5.7 and 5.9 per cent. Some manufacturers used much more talc than others for similar tablets. In some cases the excess of talc made the tablets slow in disintegration, and they were unsatisfactory, though they could hardly be described as adulterated.

J. F. LIVERSEEGE.

Legal Notes.

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

VALIDITY OF A SUMMONS UNDER THE NEW FOOD AND DRUGS ACT.

ON January 30th a summons was heard at Wimbledon against the licensee of a Wimbledon hotel, for the sale of whiskey to which 9 per cent. of water had been added.

The solicitor for the defence said that the alleged offence in this case had taken place on December 29, 1928, and he submitted that proceedings ought to have been taken under the old Act, since the new Food and Drugs Act was a consolidating or unifying Act, repealing all previous Food and Drugs Acts and part of the Licensing Act, 1921. The complainants were in the position of a person who lost the last bus; they could not apply to have the summons amended, as the stipulated period for bringing a case had elapsed.

Colonel J. Ubsdell, who appeared for the Surrey County Council, contended that the point was settled under Sec. 37 of the new Act, which said: "Every regulation, registration and sample shall have effect as if taken or given under this Act" (meaning the new Act).

The magistrates upheld the objection and dismissed the summons, but agreed to state a case for appeal.

SAND IN CINNAMON.

ON January 23rd, a firm of spice manufacturers was charged at Liverpool with giving a false warranty in respect of ground cinnamon, which had been found, on analysis, to contain 7·3 per cent. of sand and siliceous matter.

Professor Roberts, giving evidence in support of his certificate, said that genuine cinnamon should not contain any sand or siliceous matter; if any were inadvertently present, its amount should not exceed 0·5 per cent.

In cross-examination the witness admitted that in the examination of some cinnamon he had found as much as 15 per cent. of sand. A method was in use by which the sand could be removed from cinnamon, but its exact details were known only to the firm which had perfected the process. He suggested that analysts could render assistance in the matter.

The solicitor for the defence said that the defendants had done their best, and had approached people who could help, but had been unable to obtain the information. There had been previous cases in 1907 and 1924, in which the summonses had been dismissed. In face of these cases he asked whether the defendants had acted unreasonably.

A witness for the defendant firm said that he had applied to eminent Liverpool chemists, and to the Ministry of Health, and had searched the municipal libraries for information on the elimination of sand from cinnamon, but had been unsuccessful.

The Stipendiary, in discharging the defendants with a caution, said that no moral reflection on the firm was involved, but it was indisputable that the cinnamon did contain 7·3 per cent. of sand. The defendants must pay £10 10s. costs.

EXCESS OF SOLUBLE CHLORINE IN RAG FLOCK FROM COCONUT FIBRE.

ON January 15th proceedings were taken against an upholsterer, at the High Wycombe Police Court, for having in his possession flock manufactured from rags, and intended to be used for the purpose of making articles of upholstery, which did not conform to the standard of cleanliness demanded by the Rag Flock Regulations, 1912.

The sample was made from bagging and coconut fibre, and contained 243 parts of soluble chlorine per 100,000.

The case was taken under the Rag Flock Act (1911) Amendment Act, 1928, which defines "flock manufactured from rags" as being "flock which has been produced wholly or partly by tearing up woven or knitted or felted materials, whether old or new, but does not include flock obtained wholly in the process of the scouring and finishing of newly woven or newly knitted or newly felted fabrics."

There was no defence that the sample did not come within the Rag Flock Acts, 1911 and 1928, and the defendant had not protected himself by obtaining a warranty. A fine of £5 was imposed and costs.

About 5 years ago an exactly similar case came before the same Bench; a conviction was obtained, and this was upheld at Quarter Sessions, but was reversed by the High Court. (Cf. ANALYST, 1924, 49, 430.)

The effect of the Amendment Act is therefore satisfactory, as it brings this class of material within the meaning of the Act.

Ministry of Agriculture and Fisheries.

REPORT ON MUSSEL PURIFICATION.*

By R. W. DODGSON.

A MORE explanatory title of the Report would be "Purification of Shellfish as the solution of certain fishery and public health problems arising from sewage pollution; with special reference to mussels," and the book, dealing throughout with utilitarian problems, is written partly from the popular and partly from the technical point of view.

PART I.—*Section I* deals with the pollution of shellfish and its significance, with a general review of the position. Purification methods for the oyster and mussel do not depend on sterilisation, but take advantage of the capacity for self-cleansing, for mussels are diligent and successful, under favourable conditions, in getting rid of sewage and bacteria, together with particles of solid matter.

Section II describes the pathological conditions which may follow the consumption of mussels, together with the evidence supporting the view that mussels may be the cause of these conditions. Typhoid fever and other specific infections are traced to oyster and mussel infection, and experimental, epidemiological evidence is given in detail. "Mussel Poisoning" may be classified as:

(a) *Erythematous*, the familiar "musselling" of short duration, of entirely favourable prognosis, due to mussel protein, and showing a characteristic urticaria and itching.

(b) *Paralytic*, much more severe in character and derived from mussels in stagnant or foul water. Death from asphyxia may occur in a few hours, or recovery in from 2–3 to 24 hours.

(c) *Bacterial Food-poisoning Type*. Mussels, in common with almost any food, may become the vehicle of the bacteria or their toxins, or both, which are responsible for the various forms of bacterial food poisoning.

(a) and (b), although of rapid onset, with vomiting and diarrhoea as a possible common feature, are entirely distinct pathologically and chemically. The physiological action of the poison in (b) has a marked similarity to that of curare, and Brieger isolated a poisonous alkaloidal substance from poisonous mussels which he called mytilotoxine. Thesen found that, on placing normal aquaria mussels in solutions of curare and strychnine, although the mussels themselves remained healthy, their extracts soon caused symptoms of curare or strychnine poisoning or infection in rats, and such extracts added to the aquarium water of other normal mussels soon caused the latter to become poisonous. Such toxicity was fleeting. He suggests that the mussels may take in the poison from the water and destroy it, acting as scavengers. Chapman (*ANALYST*, 1926, 51, 548), after investigating the arsenic content of mussels, which in some samples was extraordinarily high, suggested that these cases might be connected with mytilotoxine poisoning. But his statement, that mytilism frequently follows the eating of mussels, suggests confusion between the (a) and (c) types of poisoning, on the one hand, and (b) on the other; and, while mytilotoxine may be responsible in some cases of (b), there appears to be strong evidence that arsenic is not. It may be mentioned that the

* Fishery Investigations. Series II. Vol. X, No. 1, 1928. H.M. Stationery Office. Price 4/1 ls. net.

popular view that poisonous properties reside in the "beard," foot and other particular parts of the mussel is erroneous.

Section III deals with the extent and significance of the pollution of shellfish beds by sewage; methods of ascertaining the existence and extent of such pollution; and measures which have been adopted or suggested for removing or mitigating the danger to the public health consequent upon such pollution.

Section IV recommends that, since the great majority, if not all, of the mussel beds in England and Wales from which mussels are taken for human consumption are polluted constantly or intermittently with sewage, and since mussels taken from any beds run serious risk of being subsequently gravely polluted by washing or storage, or both, in inshore polluted water; and, further, since it has been proved impracticable to safeguard either by relaying in unpolluted areas, by sterilising, by cooking, by any system of inspection, or by application of bacteriological standards, or by closing all polluted beds, the conclusion is that a process of purification should be applied, at once satisfactory, simple and economical, which has been in practice for 12 years at Conway, and that all home-grown and imported mussels should be thus purified.

PART II.—This deals with the work carried on at Conway, and describes the process there in use, which consists of a preliminary cleansing of the mussels by hosing, subsequent exposure overnight to a bath of sterile sea-water, draining, a second hosing, flushing, and immersing in a bath of sterile sea-water, the process being repeated a third time with a bath of 3 parts of chlorine per 1,000,000 parts of water, in which the mussels remain 1 hour, followed by draining and packing in sterilised bags. The mussels cleanse themselves inside the shell, and the chlorine is intended for sterilisation of the outside of the shell. A detailed description is given of the physiology of the mussel and of the technique employed. Mussels purified by this process should not contain more than 5 lactose-fermenting bacteria per 1 c.c., or, say, 100 per large mussel. Results of the practical operation of the plant are given, which show it as a sound economic proposition.

PART III.—*Section I* deals with certain bacteriological principles involved in the examination of shellfish, including a discussion of the question of the differentiation of "excretal" from "non-excretal" lactose-fermenting bacteria. Mussels may be regarded as polluted, either from inferential evidence, *e.g.* topographical, often sufficient in itself, or direct, *i.e.* bacteriological. The information required is usually whether the shellfish or water, or both, contain bacteria of sewage origin, and for this purpose a very large number of tests have been proposed. No bacteria definitely prove pollution to be derived from a human source, but the presence of certain ones, notably *Bacillus coli*, taken in confirmation with other circumstances, may make probability almost into certainty. Intestinal bacteria are, generally speaking, the only lactose-fermenting micro-organisms, and the differentiation of lactose fractors found in shellfish may be carried out broadly by dividing them into two main groups:—(1) The low-ratio type, giving a low gas ratio ($\text{CO}_2/\text{H}_2=1$); a positive methyl red reaction, a negative Vosges and Proskauer reaction, and (but not always) a negative Koser reaction, and (2) The high-ratio type, giving a high gas ratio ($\text{CO}_2/\text{H}_2=1.5$ or 2); methyl red negative, Vosges and Proskauer negative, and (again not always) Koser positive. Dr. W. G. Savage concludes that the presence of high-ratio organisms only is a strong indication of contamination. The name *B. coli communis* should be confined to the original bacillus so named by Escherich in 1885, and should conform to the tests given by him. Although much importance has been attached in the past to the presence or absence of *Bacillus enteritidis sporogenes* (*B. Welchii*) and streptococci as indicators of faecal pollution, their significance appears to be merely traditional,

and their presence or absence does not modify the author's views, formed as a result of the quantitatively ascertained presence (or absence) of lactose-fermentative bacilli, and one report on polluted shellfish which condemned them simply owing to the presence of these two organisms and made no mention of lactose fractors (*B. coli*), is regarded as remarkable. It may be noted that *B. Welchii* is bracketed after *B. enteritidis sporogenes*. Klein's bacillus is now considered in many quarters as hypothetical, and his culture to have consisted of *B. Welchii* and some putrefactive organism such as *B. sporogenes*, so that beyond the traditional significance there is little to justify retention of the name *B. enteritidis sporogenes*.

Section II comprises a discussion of the bacteriological methods employed by the Fishmongers' Company and certain other authorities for the examination of shellfish, and on the validity or otherwise of the interpretations placed by them on the results of the tests, and concludes by submitting:

(1) That the element of chance is of such significance that successive tests of the same shellfish, under exactly similar conditions, and with the lapse of the minimum possible amount of time between the setting up of the tests, may show widely divergent results, even to the extent of unequivocal condemnation of the shellfish, on the one hand, and unequivocal approval on the other.

(2) That the presence of glucose in the shellfish themselves or developed (or both) during the course of the test, in the shellfish substance used, may lead to entirely erroneous results, even to the extent of bringing about the condemnation of the shellfish on the apparent evidence afforded of the presence in them of bacteria of the *B. coli* group, although there may, in fact, be no such bacteria present.

(3) That, in the diagnosis of the presence or absence of bacteria of the *B. coli* group, it is unsafe to introduce, as a factor in such diagnosis, discrimination as regards the amount of gas collected during the test, except that in certain cases, where a very minute bubble of gas is in question, the shellfish may be given the benefit of the doubt.

Section III deals with the bacteriological standards of purity or impurity of shellfish.

PART IV. This gives descriptions of certain mussel-bearing areas serving as examples.

Appendix I is a note on the formation of glucose in minced mussels and oysters on incubation, by H. M. Webb.

Appendix II gives other methods of purification of shellfish.

Appendix III treats of the isolation of *Bacillus typhosus* from sewage, sewage-polluted water, and shellfish by means of glucose, sulphite, iron and bismuth, and brilliant green medium.

The text is illustrated by 15 plates, 9 figures and three maps.

D. G. H.

Connecticut Agricultural Experiment Station.

REPORT ON FOOD PRODUCTS AND DRUG PRODUCTS FOR THE YEAR 1927.

THIS is the 51st Report of the Station, and it includes the 32nd Report on Food Products and the 20th Report on Drug Products. It comprises analyses of cacao products, cereal products, fats and oils, fruit and fruit products, ice-cream, drugs,

etc., and special investigations on similar lines to those described in the previous Report (ANALYST, 1928, 52, 160).

CARBONATED BEVERAGES.—None of the 152 samples examined contained saccharin, and all exceeded the 5 per cent. of sugar required by the law. In general, the products were correctly labelled as to statements of artificial colouring matters and flavour.

UNLEAVENED BREAD.—Two samples, submitted by the dietetic department of a hospital, gave the following percentage results on analysis:

	Moisture.	Ash.	Proteins.	Fibre.	Carbohydrate.	Fat.
I.	8.02	2.13	12.13	0.17	76.95	0.60
II.	8.13	1.58	10.69	0.12	78.92	0.56

AMERICAN CHEESE.—American cheese, also known as Cheddar cheese and American Cheddar cheese, is cheese made by the Cheddar process, from heated and pressed curd obtained by the action of rennet on whole milk. It should not contain more than 39 per cent. of water, and, in the water-free substance, not less than 50 per cent. of milk fat.

Cream cheese is the unripened cheese made by the Neufchatel process from whole milk enriched with cream. It contains, in the water-free substance, not less than 65 per cent. of milk fat.

Under the laws of some states it is permissible to call cheese made from whole milk "full cream cheese." This is confusing, since cream cheese is a separate and distinct product.

Twelve samples of American cheese were examined for the Dairy and Food Commissioner. Three of these were sold as cream, or full cream, cheese, but they were evidently cheese of the Cheddar type, and the fat content, on the dry basis, corresponded to the requirements for Cheddar cheese.

The moisture in the samples examined ranged from 31 to 37.4 per cent. and the fat content, on the dry basis, ranged from 48.6 to 52.2 per cent. The average moisture was 33.4 per cent. and the average percentage of fat in the dry substance was 50.7 per cent.

LABELLING OF EGGS.—Under the State law, eggs held for more than 15 days in any place where the temperature is reduced by means of artificial refrigeration are cold storage eggs and must be designated as such when sold or offered for sale. Eggs preserved by any other artificial process must be labelled "preserved eggs."

When the price of locally gathered eggs is high and the best grades of cold storage eggs are available there is commercial advantage in offering the storage product as and for fresh eggs. Later, as prices for the two types of products become more nearly equalised the abuses cease, because there is little, if any, commercial gain to be made.

It has been estimated that only about 10 per cent. of the eggs produced are placed in cold storage. Withdrawals begin during July, and by the end of the year three-fourths or more of the total holdings may have been removed. The balance is used up by the 1st of March. The greatest abuses in the marketing of eggs occur during the autumn and early winter months.

It is evident that laboratory examinations alone cannot determine whether or not eggs are offered or sold in violation of the statute relating to cold storage eggs, but the evidence procured by such examinations, supplemented with inspection evidence, will generally lead to reasonably definite conclusions. Laboratory tests aim chiefly at determining whether or not eggs are fresh, judged by the usually accepted characteristics of fresh eggs as determined by candling, the condition of

have been proposed. One of these is Browne's formula (*A.O.A.C. Methods of Analysis*, p. 201), which is generally used in control work. The Beckman test is a qualitative test of some value, but negative results do not necessarily mean absence of commercial glucose, because some of such glucose gives no iodine reaction.

In the samples examined the differences between invert polarisations at 20° C. and at 87° C. were all between 23.2 and 26.4, with one exception, where the difference was 20.5, but in which case one of the polarisation values is questionable. The Beckmann tests were negative in all cases, but the reservation noted above must be made. Determination of glucose by means of Browne's formula indicated no considerable additions of commercial glucose. On the whole, there was no acceptable evidence of adulteration in any of the samples.

TOMATO CATSUP.—The composition now, as compared with that found in earlier examinations, may be seen from the following summary:

	1927. Per Cent.	1910. Per Cent.
Total solids (as purchased basis) ..	20.2 to 36.0	7.3 to 32.5
Salt (as purchased basis)	1.9 to 3.6	0.7 to 5.2
Salt-free ash (as purchased basis) ..	0.7 to 1.1	0.6 to 1.8
Salt-free ash (water and salt-free basis)	2.2 to 4.9	3.2 to 20.8
Insoluble solids (as purchased basis) ..	1.2 to 1.6	1.2 to 6.1
Insoluble solids (water and salt-free basis)	3.6 to 8.1	7.0 to 45.0
Protein (as purchased basis)	1.7 to 2.4	0.8 to 3.1
Protein (water and salt-free basis) ..	4.6 to 12.5	5.4 to 24.6
Fibre (as purchased basis)	0.4 to 0.6	0.3 to 0.8
Fibre (water and salt-free basis) ..	1.2 to 2.8	1.4 to 10.9

It appears that in the products recently examined the total solids exceed 20 per cent. in the material as sold, whereas in the earlier inspection many samples contained less than 20 per cent., the minimum being less than 10 per cent. Salt-free ash in the dry, salt-free material is 5 per cent. or less, whereas this was about the minimum found in earlier samples, the maximum being over 20 per cent. The percentages of protein and fibre are also distinctly lower in the recently examined products.

No standards have been adopted for tomato catsup, but on the basis of earlier analyses it appeared that reasonable limits of composition for a standard catsup might be, in the water and salt-free material, not more than 15 per cent. of insoluble solids, not more than 7 per cent. of ash, not over 4 per cent. of fibre, and not more than 12 per cent. of protein. All of the samples in the recent inspection came well within these limits.

COD-LIVER OIL VITAMIN TESTS.—*Colour Tests for Vitamin A.*—Twenty samples of cod-liver oils, mainly Norwegian medicinal oils, were submitted to the antimony trichloride test of Carr and Price, and the colour values were compared with the results of feeding tests expressed in terms of U.S.P. units. The following table shows some of the corresponding values:

Colour value of oil (approx.) ..	5	5	10	15	20	30	70
Vitamin A value (U.S.P. units) ..	250	500	250	250	500	500	1000

Two samples, each with colour values about 5, but having vitamin A values of 250 and 500 respectively, destroy the otherwise reasonably consistent correlation between the two sets of tests. The oil giving the highest value in both tests was

a sample of American oil intended only for stock-feeding purposes. A sample of "Gaduol," a so-called extract of cod-liver oil, gave a very low result in the feeding tests, and a negative result with antimony chloride.

Colour Tests for Vitamin D.—Shear's test (*Proc. Soc. Exp. Biol. and Med.*, **23**, 546) was tried on a number of samples. It was found that cottonseed oil may give a colour not readily distinguishable from that produced by cod-liver oil, and the green shade stated to be characteristic of cod-liver oil was not observed. Rosenheim and Webster (*Biochem. J.*, **20**, 544) have found that the Shear test is given by substances which are inactive as regards vitamin D, and also by certain organic peroxides.

"DENICOTINISED" TOBACCO.—Enquiries from physicians and others regarding the merits of so-called "denicotinised" tobaccos, or tobacco products for which reduced nicotine content is claimed or inferred by the label, have led to the examination of as many of these products as could be obtained.

The usual method by which denicotinised tobaccos are prepared is essentially a re-sweating process accomplished by treatment with superheated steam or by heating in vacuum chambers. Dixon (*Brit. Med. J.*, Oct. 1927) cites the use of solvents for removing nicotine and other objectionable constituents. It is conceivable also that diluents consisting of non-nicotine-containing leaves foreign to tobacco might be used, but no attempt was made in this investigation to detect the presence of such foreign material.

The terms "processed" and "unprocessed," frequently used in this discussion, refer to the special re-sweating treatment employed to reduce nicotine content. It is understood, of course, that all tobacco undergoes various processes in the course of its preparation for commercial purposes.

None of the brands examined were claimed to be nicotine-free. However, such terms as "denicotinised" and "denicotined" were generally construed to mean "practically free from nicotine," particularly if the further assurance is given, or implied, that the consumer may smoke as much as he likes of these processed tobaccos. To such declarations as "bulk of nicotine removed" or "reduced nicotine content" less objection can be raised; from the first statement we should expect that over one-half of the original nicotine had been removed, while any reduction at all in nicotine would suffice to make the second declaration one of fact. The obvious difficulty in judging whether or not these statements are true lies in the lack of information as to the amount of nicotine in the various tobaccos before they were processed. No average figure for the nicotine content of tobacco in general can be given, because wide differences occur due to varieties of leaf and varied conditions of culture and growth. There may be substantial differences also among the leaves of the same plant, dark (upper) leaves showing higher nicotine content than leaves lower down on the stalk (lights and seconds).

From an examination of data from analyses of ordinary tobacco (given in a series of tables) and "denicotinised" products the following comparative summary has been drawn up:

				Nicotine in ordinary tobaccos. moisture-free. (58 analyses.) Per Cent.	Nicotine in "Denicotinised" tobaccos. moisture-free (17 analyses.) Per Cent.
Maximum	3.63	2.73
Minimum	0.47	0.74
Average	1.96	1.41

From this summary it is clear that, on the basis of averages, these "denicotinised" products, as a group, contain about 30 per cent. less nicotine than is likely to be found in ordinary unprocessed tobaccos. If we may assume 2 per cent. as a fair approximation of the average nicotine content (dry basis), which may be expected in the various forms of ordinary smoking tobaccos, a reference to the analyses showed that four "denicotinised" samples contained more than this average, and that four contained less than one-half as much. For the remainder, it seems fair to conclude that approximately one third to one half of the original nicotine had been removed.

It is of interest to compare these processed tobaccos, so far as possible, with ordinary tobaccos of corresponding types on the basis of nicotine content, assuming, as fairly representative nicotine values, 2.5 to 3.5 per cent. for Virginia tobacco, 2.0 to 3.0 per cent. for various other domestic leaf, 1.1 to 2.4 per cent. for Havana, and 1.0 to 1.5 per cent. for Turkish.

Another comparison may be made on the basis of the classes of products examined. The unprocessed cigarettes, as shown by analyses, have a range of nicotine content from 1.1 to 3.2 per cent., whereas "denicotinised" cigarettes range from 1.2 to 2.7 per cent. Pipe tobacco, unprocessed, ranges from 1.6 to 2.3 per cent., as compared with 1.1 to 2.5 per cent. for the denicotinised article. The data on cigars are rather limited, but the range is 1.3 to 2.1 for ordinary cigars and 0.7 to 1.4 per cent. for processed cigars.

From these data it is quite obvious that, in general, the denicotinised products here represented contained but little less nicotine than do ordinary tobaccos of corresponding leaf types. Notwithstanding considerable reductions which may be indicated in certain instances, it is not difficult to find among ordinary tobaccos brands in which nicotine is not greatly in excess of that present in the most thoroughly "processed" of these denicotinised products.

Parliamentary Notes.

CHLORINE TREATMENT OF FLOUR.

ON January 28th the Minister of Health was asked by Lt.-Col. Heneage if his attention had been called to the use of chlorine for improving certain inferior grades of foreign flour, and if so, whether he proposed to take any action in the matter.

Sir Kingsley Wood, replying, said that the Minister was aware that chlorine was sometimes used for treating foreign flours, but that he understood that its use was diminishing. In these circumstances, and in view of the danger of increasing the cost of bread, and of driving the milling trade abroad, he did not propose at present to take any action.

POISONING BY NITROGLYCERIN.

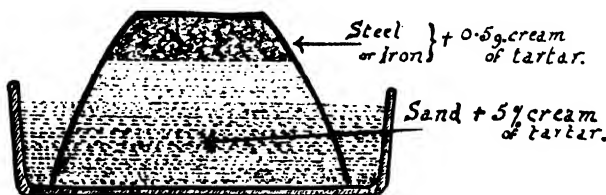
ON January 24, the Minister of War was asked in the House of Commons, if his attention had been called to the death of a research worker at Woolwich Arsenal; whether it had been established that the death was due to the fumes of nitroglycerin; and what action he proposed to take to prevent the future occurrence of such fatalities.

Mr. Cooper replied that he had seen a report of the inquest at which the Coroner, in his verdict, stated that death was accelerated by the deceased having come into contact with the fumes of some chemical poison allied to nitroglycerin. The Minister of War was advised that poisoning by nitroglycerin was an extremely rare occurrence, and might imply an individual predisposition which could not be foreseen. Instructions had been issued directing any worker who felt indisposed as a possible result of contact with the materials he was using, to report the fact at once to his superior.

The Determination of Sulphur by the Evolution Process in Steels and Cast Iron.

THE organisers of the British Chemical Standards Movement have for some time pointed out that all carbon steels and cast iron in the form of millings, drillings, etc., after being in contact with air for a considerable period—usually at least two years—cease to yield the full quantity of sulphur as sulphide when dissolved in hydrochloric acid, even when they have been stored in a sealed container, and still remain bright. The result in such a case is that the standard value for sulphur, as determined by the evolution process, is low; and this can only be remedied by annealing the drillings, etc., in an oxygen-free atmosphere, such as carbon dioxide or nitrogen, before making the determination. This is not ordinarily carried out with ease in a works laboratory, and the following simple annealing process has therefore been devised:

Five grms. of the drillings are mixed with 0.5 gram. of dry powdered cream-of-tartar, placed in a porcelain crucible ($1\frac{5}{8}$ in. diameter at the top, and $\frac{3}{4}$ in. high),



which is then filled to the brim with a mixture of 95 per cent. of acid-washed, 40-mesh, calcined sea-sand, and 5 per cent. of powdered cream-of-tartar. On it is placed a silica capsule, $1\frac{1}{4}$ in. internal diameter and $\frac{1}{2}$ in. deep. The crucible is inverted, and the space on the outside, between the crucible and the capsule, is filled with the mixture of sand and tartar, as shown in the diagram.

The crucible is inserted gradually into a muffle at 750 to 850° C. (not hotter or the glaze may be badly attacked), and when pushed completely in, it is heated for 20 minutes, after which it is taken out and cooled on an iron plate, and the entire contents transferred to a sulphur flask, and sulphur is evolved as usual, by means of hot strong hydrochloric acid (sp. gr. 1.26).

A blank test should be made with the reagents, to insure that they do not yield any sulphur as sulphide when treated according to the test. Cream-of-tartar is usually free from sulphur, but sand, even after washing, has been found to contain a little, which will be reduced to sulphide and for which an allowance must be made.

The accuracy of the process has been established after carefully making a number of tests on different standards. White irons and certain alloy steels which do not yield all their sulphur as sulphide by direct evolution may also be treated successfully by this method.

As further confirmation of the application of the method for white irons, it has been submitted to two different chemists experienced in the analysis of these irons—namely, Mr. R. D. Dick of Messrs. Pease & Partners, Ltd., Normanby Iron Works, Middlesbrough, and Mr. A. E. Peace of Messrs. Leys Malleable Castings, Ltd., Derby, and in each case several tests on white iron have given results in close agreement with those obtained by the gravimetric method, whilst the ordinary evolution process, without annealing, has given low results.

Annealing with cream-of-tartar, etc., has, of course, been recommended for years, but the methods of carrying it out have not been satisfactory on account of the uncertainty of ensuring complete freedom from oxidation. The only new feature about this method is the simple and sure means employed to avoid oxidation.

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Statutory Rules and Orders.

1928, No. 571.

MERCHANDISE MARKS.

THE MERCHANDISE MARKS (IMPORTED GOODS) No. 3 ORDER, 1928.*

At the Court at Buckingham Palace, the 13th day of July, 1928.

Present: The King's Most Excellent Majesty in Council.

Whereas by sub-section (1) of Section 2 of the Merchandise Marks Act, 1926 (16 & 17 Geo. 5, c. 53), it is provided that after an enquiry in relation to goods of any class or description has on a reference from the appropriate department been held by a committee appointed for the purposes of the said Act, and the report of the committee on the matter has been taken into consideration by the department, that department may, unless it appears to them that the trade of the United Kingdom or the trade generally of other parts of His Majesty's Dominions with the United Kingdom would be prejudiced if imported goods of that class or description for use or consumption in the United Kingdom were prohibited to be sold unless they bear an indication of origin, make a representation to His Majesty that it is desirable that an Order should be made under the said Section 2, and His Majesty in Council may thereupon, subject to the provisions of the said Act, make an Order prohibiting the sale or exposure for sale in the United Kingdom of imported goods of that class or description unless they bear an indication of origin:

And whereas in accordance with the provisions of the said section enquiries in relation to (a) Honey, and (b) Fresh apples, have on references from the appropriate department, namely the Minister of Agriculture and Fisheries, the Secretary of State for the Home Department, and the Secretary of State for Scotland acting jointly (hereinafter called "the Department") been held by a committee appointed for the purposes of the said Act and the reports of that committee have been taken into consideration by the Department:

And whereas by sub-section (5) of Section 2 of the said Act it is provided that if on an enquiry under sub-section (1) of the said section it appears to a committee to be desirable that any imported goods should bear an indication of origin at the time of importation, and the committee so reports to the appropriate department, that department unless, having regard to all the circumstances of the case including the re-export trade of the United Kingdom in that class or description of goods, it considers such action undesirable, may make a representation to His

Majesty that the goods should bear an indication of origin at the time of importation, and His Majesty may by Order in Council under the said section (without prejudice to His powers under sub-section (1) of the said section) make provision accordingly:

And whereas it does not appear to the Department that the trade of the United Kingdom or the trade generally of other parts of His Majesty's Dominions with the United Kingdom would be prejudiced if the goods which were the subject of the said enquiries and are described in Parts I and II of this Order imported for use or consumption in the United Kingdom were prohibited to be sold unless they bear an indication of origin, and the Department has accordingly made representations to His Majesty that it is desirable that an Order should be made under the said Section 2:

And whereas the committee has reported to the Department that it appears to them to be desirable that such of the said goods as are described in Part II of this Order should bear an indication of origin at the time of importation:

And whereas the Department having had regard to all the circumstances of the case, including the re-export trade in those goods, has made representations to His Majesty that it is desirable that such of the said goods as are described in Part II of this Order should bear an indication of origin at the time of importation:

And whereas by sub-section (2) of Section 10 of the said Act, it is provided that an Order in Council made under the foregoing provisions of the Act with respect to goods of any class or description shall not extend to blends or mixtures consisting of or containing those goods unless the Order expressly so provides and, where any Order in Council so provides, the indication of origin to be given in respect of the blends or mixtures shall, notwithstanding anything in the said Act, be an indication in such form as the Order prescribes;

Now, therefore, His Majesty, by and with the advice of His Privy Council, in pursuance of the powers vested in Him by the said Act, and of all other powers enabling Him in that behalf, is pleased to order, and it is hereby ordered, as follows:—

PART I.—(*Honey*).

1. It shall not be lawful to sell or expose for sale in the United Kingdom any imported honey, or any blend or mixture of honeys of which imported honey forms part, unless it bears an indication of origin.

2. The indication of origin shall be printed, stencilled, stamped or branded on the container, or on a label securely attached thereto, indelibly and in a conspicuous manner, in plain block letters not less than one-twelfth of an inch in height when the greatest dimension of the package does not exceed six inches, and not less than one-eighth of an inch in height when the greatest dimension of the package exceeds six inches. For the purpose of this Part of this Order the expression "greatest dimension" shall mean the height, length or breadth, whichever is the greatest, of a rectangular or approximately rectangular package, and the height or maximum diameter, whichever is the greater, of a cylindrical, oval or conical package.

3. The form of the indication of origin in the case of blends or mixtures containing imported honey shall be, at the option of the person applying the indication, either:—(a) in the case of honey derived entirely from countries within the Empire, the word "Empire"; and, in the case of honey derived entirely from foreign countries, the word "Foreign"; or (b) a definite indication of all the countries of origin of the honeys forming the blend or mixture; or (c) the words "Blended imported"; provided that the indication "Blended imported" shall be applicable to any blend or mixture of honey, even though it contain honey produced in the United Kingdom.

4. This Part of this Order shall not apply to exposure for sale wholesale if the person exposing the goods is a wholesale dealer.

5. The provisions of this Part of this Order shall come into force at the expiration of six months from the date hereof.

PART II.—(*Fresh Apples*).

6. Subject as hereinafter provided, it shall not be lawful to import any fresh apples into the United Kingdom, nor to sell or expose for sale in the United Kingdom, any imported fresh apples unless they bear an indication of origin.

7. The indication of origin shall be marked indelibly and in a conspicuous manner as follows:—(a) On importation, on exposure for sale wholesale and on sale, by means of printing, stencilling, stamping or branding on each outer container, or on a label securely attached thereto, in letters not less than half an inch in height. (b) On exposure for sale by retail, by means of a show-ticket, clearly visible to intending purchasers, bearing the indication of origin in letters not less than half an inch in height.

8. This Part of this Order shall apply on exposure for sale wholesale whether the person exposing the goods is or is not a wholesale dealer.

9. Nothing in this Part of this Order shall apply to sales of fresh apples in quantities of fourteen pounds or less.

10. The provisions of this Part of this Order shall come into force at the expiration of four months from the date hereof.

PART III.—(General).

11.—(a) This Order may be cited as The Merchandise Marks (Imported Goods) No. 3 Order, 1928;

(b) The Interpretation Act, 1889,* shall apply to the interpretation of this Order as if it were an Act of Parliament.

M. P. A. HANKEY.

1928, No. 1052.

MERCHANDISE MARKS.

THE MERCHANDISE MARKS (IMPORTED GOODS) No. 5 ORDER, 1928.†

At the Court at Buckingham Palace, the 21st day of December, 1928.

Present: Her Majesty the Queen, His Royal Highness the Prince of Wales, His Royal Highness the Duke of York, Archbishop of Canterbury, Lord Chancellor, Prime Minister, Lord Chamberlain, Secretary Sir W. Joynson Hicks, Hon. Walter Guinness.

Whereas His Majesty was pleased by His Commission dated the 4th day of December, 1928, to nominate and appoint Her Majesty the Queen, His Royal Highness the Prince of Wales, K.G., K.T., K.P., G.C.S.I., G.C.M.G., G.C.I.E., G.C.V.O., G.B.E., His Royal Highness the Duke of York, K.G., K.T., G.C.V.O., the Most Reverend Father in God Cosmo Gordon, Archbishop of Canterbury, the Right Honourable Douglas McGarel, Baron Hailsham, Lord High Chancellor of Great Britain, and the Right Honourable Stanley Baldwin, Prime Minister and First Lord of the Treasury, or any three of them, during His Majesty's illness, to summon and hold on His Majesty's behalf His Privy Council, and to signify thereat His Majesty's approval of any matter or thing to which His Majesty's approval in Council is required:

And whereas by sub-section (1) of Section 2 of the Merchandise Marks Act, 1926 (16 & 17 Geo. 5, c. 53), it is provided that after an enquiry in relation to goods of any class or description has on a reference from the appropriate department been held by a committee appointed for the purposes of the said Act, and the report of the committee on the matter has been taken into consideration by the department, that department may, unless it appears to them that the trade of the United Kingdom or the trade generally of other parts of His Majesty's Dominions with the United Kingdom would be prejudiced if imported goods of that class or description for use or consumption in the United Kingdom were prohibited to be sold unless they bear an indication of origin, make a representation to His Majesty that it is desirable that an Order should be made under the said Section 2, and His Majesty in Council may thereupon, subject to the provisions of the said Act, make an Order prohibiting the sale or exposure for sale in the United Kingdom of imported goods of that class or description unless they bear an indication of origin:

And whereas in accordance with the provisions of the said section enquiries in relation to (a) Currants, Sultanas and Raisins; (b) Eggs in shell and Dried Eggs; and (c) Oat Products have on references from the appropriate department, namely the Minister of Agriculture and Fisheries, the Secretary of State for the Home Department, and the Secretary of State for Scotland acting jointly (hereinafter called "the Department") been held by a committee appointed for the purposes of the said Act and the reports of that committee have been taken into consideration by the Department:

And whereas by sub-section (5) of Section 2 of the said Act it is provided that if on an enquiry under sub-section (1) of the said section it appears to a committee to be desirable that any imported goods should bear an indication of origin at the time of importation, and the committee so reports

* 52-3 V. c. 63.

† H.M. Stationery Office. Price 2d. net.

to the appropriate department, that department unless, having regard to all the circumstances of the case including the re-export trade of the United Kingdom in that class or description of goods, it considers such action undesirable, may make a representation to His Majesty that the goods should bear an indication of origin at the time of importation, and His Majesty may by Order in Council under the said section (without prejudice to His powers under sub-section (1) of the said section) make provision accordingly:

And whereas it does not appear to the Department that the trade of the United Kingdom or the trade generally of other parts of His Majesty's Dominions with the United Kingdom would be prejudiced if the goods which were the subject of the said enquiries and are described in Parts I to IV of this Order imported for use or consumption in the United Kingdom were prohibited to be sold unless they bear an indication of origin, and the Department has accordingly made representations to His Majesty that it is desirable that an Order should be made under the said Section 2:

And whereas the Committee has reported to the Department that it appears to them to be desirable that the said goods should bear an indication of origin at the time of importation:

And whereas the Department having had regard to all the circumstances of the case, including the re-export trade in those goods, has made representations to His Majesty that it is desirable that the said goods should bear an indication of origin at the time of importation:

And whereas by sub-section (2) of Section 10 of the said Act, it is provided that an Order in Council made under the foregoing provisions of the Act with respect to goods of any class or description shall not extend to blends or mixtures consisting of or containing those goods unless the Order expressly so provides and, where any Order in Council so provides, the indication of origin to be given in respect of the blends or mixtures shall, notwithstanding anything in the said Act, be an indication in such form as the Order prescribes:

Now, therefore, Her Majesty the Queen, His Royal Highness the Prince of Wales, His Royal Highness the Duke of York, His Grace the Archbishop of Canterbury, the Lord High Chancellor of Great Britain, and the Prime Minister and First Lord of the Treasury, being authorised thereto by His Majesty's said Commission, in pursuance of the powers vested in them by the said Act, and of all other powers enabling them in that behalf, by and with the advice of His Majesty's Privy Council, on His Majesty's behalf are pleased to order, and it is hereby ordered, as follows:—

PART I.—(*Currants, Sultanas and Raisins*).

1. Subject as hereinafter provided, it shall not be lawful to import any currants, sultanas or raisins into the United Kingdom, nor to sell or expose for sale in the United Kingdom any imported currants, sultanas or raisins, unless they bear an indication of origin.

2. The indication of origin shall be marked indelibly and in a conspicuous manner as follows:—(a) On importation, on exposure for sale wholesale and on sale, by means of printing, stencilling, stamping or branding on each outer container, or on a label securely attached thereto, in letters not less than half an inch in height.

(b) On exposure for sale by retail—(i) in the case of currants, sultanas or raisins not prepacked for sale by retail either on the premises where they are exposed for sale or otherwise, by means of a show ticket, clearly visible to intending purchasers, bearing the indication of origin in letters not less than half an inch in height; (ii) in the case of currants, sultanas or raisins prepacked for sale by retail, save as provided in paragraph 3 (b) of this Order, by means of printing on or printed labels affixed to each package bearing the indication of origin in plain block letters not less than one-twelfth of an inch in height when the greatest dimension of the package does not exceed six inches, and not less than one-eighth of an inch in height when the greatest dimension of the package exceeds six inches.

3. Nothing in this Part of this Order shall require imported currants, sultanas or raisins to bear an indication of origin:—(a) On importation as samples not exceeding one pound in weight; (b) On exposure for sale by retail in packages made up for sale on the premises of a retailer; or (c) On sale when sold in quantities not exceeding fourteen pounds in weight.

4. The provisions of this Part of this Order so far as they relate to marking on importation shall come into force at the expiration of four months from the date hereof, and so far as they relate to marking on exposure for sale and sale at the expiration of six months from the date hereof.

PART II.—(*Eggs in Shell*).

5. It shall not be lawful to import any hen or duck eggs in shell into the United Kingdom, nor to sell or expose for sale in the United Kingdom any imported hen or duck eggs in shell, unless they bear an indication of origin.

6. The indication of origin shall be conspicuously and durably marked in ink on the shell of each imported egg in letters not less than two millimetres in height.

7. The provisions of this Part of this Order shall come into force at the expiration of four months from the date hereof.

PART III.—(*Dried Eggs*).

8. Subject as hereinafter provided, it shall not be lawful to import any dried eggs into the United Kingdom, nor to sell or expose for sale in the United Kingdom any imported dried eggs, unless they bear an indication of origin.

9. The indication of origin shall be marked indelibly and in a conspicuous manner as follows:—*(a)* On importation, by means of printing, stencilling, stamping or branding on each outer container, or on a label securely attached thereto, in letters not less than half an inch in height. *(b)* On exposure for sale, wholesale or by retail, and on sale, save as provided in paragraph 10 of this Order, by means of printing, stencilling, stamping or branding on each container, or on a label securely attached thereto, in plain block letters not less than one-twelfth of an inch in height when the greatest dimension of the package does not exceed six inches, and not less than one-eighth of an inch in height when the greatest dimension exceeds six inches.

10. Nothing in this Part of this Order shall require imported dried eggs to bear an indication of origin when sold or exposed for sale by retail otherwise than in packages which are made up before reaching the retailer.

11. The provisions of this Part of this Order shall come into force at the expiration of three months from the date hereof.

PART IV.—(*Oat Products*).

12. For the purpose of this Part of this Order, the expression "oat products" shall mean oatmeal, rolled oats (but not crushed or bruised natural oats), oat flour and groats.

13. Subject as hereinafter provided, it shall not be lawful to import into the United Kingdom any oat products, nor to sell or expose for sale in the United Kingdom any imported oat products, unless they bear an indication of origin.

14. The provisions of this Part of this Order shall extend to all blends or mixtures of oat products which consist of or contain imported oat products.

15. The indication of origin shall be marked indelibly and in a conspicuous manner as follows:—

(a) On importation, on exposure for sale wholesale and on sale, by means of printing, stencilling, stamping or branding on each outer container, or on a label securely attached thereto, in letters not less than half an inch in height.

(b) On exposure for sale by retail—*(i)* in the case of oat products not prepacked for sale by retail, by means of a show ticket, clearly visible to intending purchasers, bearing the indication of origin in letters not less than half an inch in height; *(ii)* in the case of oat products, prepacked, before importation, for sale by retail, by means of printing or stamping on each package, or on a label securely attached thereto, in plain block letters not less than one-twelfth of an inch in height when the greatest dimension of the package does not exceed six inches and not less than one-eighth of an inch in height when the greatest dimension of the package exceeds six inches; and *(iii)* in the case of oat products prepacked, after importation, for sale by retail, either by means of a show ticket, as in *(i)* above, or by means of marking on each package, as in *(ii)* above, at the option of the person applying the indication.

16. The form of the indication of origin in the case of blends or mixtures of oat products which consist of or contain imported oat products shall be, at the option of the person applying the indication, either:—*(a)* in the case of oat products derived entirely from within the Empire the word "Empire"; and, in the case of oat products derived entirely from foreign countries, the word "Foreign"; or *(b)* a definite indication of all the countries of origin of the oat products forming the blend or mixture; or *(c)* the words "Blended imported." Provided that the indication "Blended imported" shall be applicable to any blend or mixture of oat products containing imported oat products even though it also contain oat products produced in the United Kingdom.

17. Nothing in this Part of this Order shall require imported oat products to bear an indication of origin on sale when sold in quantities of fourteen pounds or less.

18. The provisions of this part of this Order so far as they relate to marking on importation shall come into force four months from the date hereof and, so far as they relate to marking on exposure for sale and sale at the expiration of six months from the date hereof.

PART V.—(*General*).

19. Parts I, II, III, and IV of this Order shall apply on exposure for sale wholesale whether the person exposing the goods is or is not a wholesale dealer.

20. For the purpose of paragraphs 2, 9 and 15 of this Order, the expression "greatest dimension" shall mean the height, length or breadth, whichever is the greatest, of a rectangular or approximately rectangular package, and the height or maximum diameter, whichever is the greater, of a cylindrical, oval or conical package.

21. (a) This Order may be cited as "The Merchandise Marks (Imported Goods) No. 5 Order, 1928."

(b) The Interpretation Act, 1889,* shall apply to the interpretation of this Order as if it were an Act of Parliament.

M. P. A. HANKEY.

1928, No. 984.

AGRICULTURAL PRODUCE (GRADING AND MARKING).†

THE AGRICULTURAL PRODUCE (GRADING AND MARKING) (EGGS) REGULATIONS, 1928, DATED DECEMBER 15, 1928, MADE BY THE MINISTER OF AGRICULTURE AND FISHERIES AS TO GRADE DESIGNATIONS AND GRADE DESIGNATION MARKS FOR EGGS PRODUCED IN ENGLAND AND WALES AND AS TO THE MARKING OF EGGS WHICH HAVE BEEN SUBJECTED TO ANY PROCESS OF PRESERVATION.

In exercise of the powers conferred on him by the Agricultural Produce (Grading and Marking) Act, 1928, the Minister of Agriculture and Fisheries hereby makes the following regulations:—

1. Grade designations to indicate the quality of hen eggs produced in England and Wales shall be as follows:—Special, Standard, Pullet Standard; and the quality indicated by such grade designations shall be deemed to be as defined in columns (2) and (3) of the First Schedule hereto.

2. Grade designations to indicate the quality of duck eggs produced in England and Wales shall be as follows:—Special (Duck), Standard (Duck), Ducklet Standard; and the quality indicated by such grade designations shall be deemed to be as defined in columns (2) and (3) of the Second Schedule hereto.

3. A grade designation mark shall be any one of the grade designations specified in regulations (1) and (2) above associated with the words "Empire Buying Begins at Home" and with the following mark, namely, a map of England and Wales in silhouette with the words "Produce of England and Wales" inscribed in a circle placed centrally in the map within which circle is a design representing the Union Jack and which is more particularly described in the Third Schedule hereto.

4. After the twenty-eighth day of February, nineteen hundred and twenty-nine, any egg to which Section 3 of the aforesaid Act applies shall be marked conspicuously and legibly on the shell with the word "PRESERVED" in letters of not less than $\frac{1}{16}$ inch in height, the word being enclosed in a circle of not less than $\frac{1}{4}$ inch diameter.

5. If and so long as any Order in Council made under Section 2 of the Merchandise Marks Act, 1926, is in force prohibiting the sale or the exposure for sale in the United Kingdom of imported eggs unless they bear an indication of origin, any British egg which has been kept in cold storage or chemical storage shall, in the former case, be marked conspicuously and legibly on the shell with the word "CHILLED" or with the words "COLD STORED" and, in the latter case, with the word "STERILISED," the letters being in each case not less than $\frac{1}{16}$ inch in height and the word or words being enclosed in a circle of not less than $\frac{1}{4}$ inch diameter.

6. When any person applies for the registration of premises to be used by way of trade or for purposes of gain for the cold storage or chemical storage of eggs, the Council of the County or County Borough, or, as respects the administrative County of London, the Common Council of the City of London and the Council of every Metropolitan Borough, in which the premises are

* 52-3 V. c. 63.

† H.M. Stationery Office. Price 1d. net.

situated shall enter in a register the name and address of the person and the address of the premises and shall forward a copy of each such entry to the Ministry of Agriculture and Fisheries and shall issue a certificate of registration to the person making the application.

7. These regulations may be cited as the Agricultural Produce (Grading and Marking) (Eggs) Regulations, 1928.

In Witness whereof the Official Seal of the Minister of Agriculture and Fisheries is hereunto affixed this fifteenth day of December, 1928.

(L.S.)

CHARLES J. H. THOMAS.

SCHEDULE I.

HEN EGGS PRODUCED IN ENGLAND AND WALES: GRADE DESIGNATIONS AND DEFINITIONS OF QUALITY.

Grade designation. (1)	Definitions of quality.	
	Minimum weight. (2)	State or condition. (3)
SPECIAL	oz. 2½	{ First Quality, <i>i.e.</i> the egg must not have been preserved by any process, the shell must be clean and sound, the yolk translucent or faintly but not clearly visible, the white translucent and firm, and the air-space must not exceed ¼ inch in depth.
STANDARD	2	
PULLET STANDARD ..	1½	

SCHEDULE II.

DUCK EGGS PRODUCED IN ENGLAND AND WALES: GRADE DESIGNATIONS AND DEFINITIONS OF QUALITY.

Grade designation. (1)	Definitions of quality.	
	Minimum weight. (2)	State or condition. (3)
SPECIAL (DUCK) ..	oz. 2½	{ First Quality, <i>i.e.</i> the egg must not have been preserved by any process, the shell must be clean and sound, the yolk visible but not dense and moving slowly when the egg is rotated, and the white must be translucent and firm.
STANDARD (DUCK) ..	2½	
DUCKLET STANDARD ..	2¼	

SCHEDULE III.

GRADE DESIGNATION MARK.

The mark hereunder shown shall be a grade designation mark when used in association with a grade designation and with the words "Empire Buying Begins at Home."

MARKING OF PRESERVED EGGS; EGG GRADING REGULATIONS, etc.

The Minister of Agriculture and Fisheries has made an Order under Section 3 of the Agricultural Produce (Grading and Marking) Act, 1928, exempting from the operation of that Section eggs preserved by cold storage and chemical storage. The reason for this Order is that it is not possible to ascertain by analysis whether eggs have, in fact, been kept in cold storage or chemical

storage. The effect of the Order, therefore, is to limit the operation of Section 3 to eggs preserved by methods such as immersion in lime-water, water-glass or oil; all eggs so preserved, whether home-produced or imported, must, after February 28th, 1929 (the date fixed by the Act), be marked in the prescribed manner on sale or exposure for sale.

Section 4 of the Act requires that British eggs which have been cold-stored or chemically stored should be marked before they leave the storage premises, but this Section only becomes operative if and so long as an Order in Council is enforced under the Merchandise Marks Act, 1926, prohibiting the sale or exposure for sale of imported eggs unless they bear an indication of origin.

The Minister has prepared draft regulations under Sections 1, 2, 3, and 4 of the Act prescribing (a) grade designations and grade designation marks for hen and duck eggs, (b) the way in which eggs preserved by any process, including cold storage and chemical storage, shall be marked, and (c) the method by which premises used for the cold storage or chemical storage of eggs shall be registered by Local Authorities responsible for the enforcement of the Statute. Copies of these draft regulations, known as the Agricultural Produce (Grading and Marking) Draft (Egg) Regulations, 1928, can be obtained from His Majesty's Stationery Office, Adastral House, Kingsway, London, W.C.1, price 1d.

MINISTRY OF AGRICULTURE AND FISHERIES,
10, WHITEHALL PLACE, LONDON, S.W.1.
16th October, 1928.

Reconstituted Cream Bill.

A BILL TO REGULATE THE SALE AND MANUFACTURE OF RECONSTITUTED CREAM.*

Be it enacted by the King's most Excellent Majesty, by and with the advice and consent of the Lords Spiritual and Temporal, and Commons, in this present Parliament assembled, and by the authority of the same, as follows:—1.—(1) Reconstituted cream shall not be sold or offered or exposed for sale for human consumption under any description or designation including the word "cream" unless that work is immediately preceded by the word "reconstituted." (2) Every receptacle used for the conveyance of reconstituted cream for sale for human consumption, or containing reconstituted cream at any time when it is exposed for such sale, shall have the words "reconstituted cream" printed in large and legible type either on the receptacle itself or on a label securely attached thereto. (3) If any person contravenes any of the provisions of this section he shall be guilty of an offence against this Act.

2.—(1) Reconstituted cream shall not be manufactured, sold or exposed or kept for sale for human consumption except at premises registered with the Food and Drugs Authority:

Provided that this requirement shall not apply—(a) to the manufacture of reconstituted cream solely for consumption on the premises on which it is manufactured or for use in the preparation on those premises of some other article of good; or (b) to the sale, exposure or keeping for sale of reconstituted cream on any premises where it is sold or exposed or kept for sale for consumption on those premises only or is not supplied otherwise than in the properly closed and unopened receptacles in which it was delivered to those premises.

(2) The Food and Drugs Authority shall keep a register of premises under this section, and shall on application being made by the owner or occupier of any premises enter the premises in the register and shall from time to time revise the register as occasion may require.

(3) Any officer of the Food and Drugs Authority duly authorised in that behalf by the authority may at all reasonable times enter and inspect any premises registered with the authority under this section.

(4) If a justice of the peace is satisfied by information on oath that there is reasonable ground for supposing that any unregistered premises are being used for the manufacture of reconstituted cream contrary to the provisions of this section, he may grant a search warrant authorising any

* [Bill 34; 19 Geo. 5.] Ordered by the House of Commons to be printed, January 24, 1929. To be purchased from H.M. Stationery Office. Price 2d. net.

such officer as aforesaid to enter and inspect the premises and to search for and seize any machine suitable for use in the manufacture of reconstituted cream.

(5) If any person uses any unregistered premises for the manufacture or sale of reconstituted cream in contravention of this section, or obstructs any such officer as aforesaid in the execution of his powers under this section, or fails to give any such officer all reasonable assistance in his power, or to furnish him with any information he may reasonably require, he shall be guilty of an offence against this Act.

3. Such of the provisions of the Public Health Acts, 1875 to 1926 (or, in London, the Public Health (London) Acts, 1891 to 1926), and the Milk and Dairies (Consolidation) Act, 1915, and of any order or regulation made under any of those Acts, as relate to cream (other than those relating to registration) shall apply to reconstituted cream.

4. It shall be the duty of every Food and Drugs Authority to enforce the provisions of this Act, and any expenses incurred by the authority for that purpose shall be defrayed as expenses under the Food and Drugs (Adulteration) Act, 1928:

Provided that this section shall not apply to such of the provisions of any Act, order or regulation applied by this Act as are enforceable by any other authority.

5.—(1) If any person commits an offence against this Act he shall be liable on summary conviction to a fine not exceeding, in the case of a first offence, five pounds, in the case of a second or subsequent offence, fifty pounds, and in any case where the offence is a continuing offence, to a further fine not exceeding forty shillings for each day during which the offence continues.

(2) For the purposes of proceedings under this Act—(a) where reconstituted cream is sold or offered exposed or kept for sale, it shall be presumed to be sold or offered exposed or kept for sale for human consumption unless the contrary is proved; (b) where any article having the composition of cream or reconstituted cream is sold or exposed or kept for sale on premises registered under this Act, it shall be presumed to be reconstituted cream unless the contrary is proved.

(3) The provisions of subsection (6) of section twenty-seven and of sections twenty-nine and thirty of the Food and Drugs (Adulteration) Act, 1928, relating to offences and warranties under that Act, as set out with the appropriate modifications in the schedule to this Act, are hereby incorporated with this Act and shall apply to proceedings under this Act.

6. In this Act—"Food and Drugs Authority" has the same meaning as in the Food and Drugs (Adulteration) Act, 1928; "Cream" means that portion of milk rich in milk fat which has been separated by skimming or otherwise; "Reconstituted cream" means an article of food resembling cream and containing no ingredient which is not derived from milk except water or any ingredient or material which may lawfully be contained in an article sold as cream.

7. This Act shall apply to Scotland subject to the following modifications—(a) The following section shall be substituted for section three—Such of the provisions of the Milk and Dairies (Scotland) Act, 1914, and of any order, regulation or bye-law made under that Act as relate to cream (other than those relating to registration) shall apply to reconstituted cream: (b) The expression "defendant" shall mean respondent, and the expression "information" shall mean "complaint."

8.—(1) This Act may be cited as the Reconstituted Cream Act, 1929. (2) This Act shall come into operation on the first day of June, nineteen hundred and twenty-nine. (3) This Act shall not extend to Northern Ireland.

SCHEDULE.

PROVISIONS OF FOOD AND DRUGS (ADULTERATION) ACT, 1928, APPLIED.

1. Where an employer is charged with an offence against this Act, he shall be entitled, upon information duly laid by him, to have any other person whom he charges as the actual offender brought before the court at the time appointed for hearing the charge, and if, after the commission of the offence has been proved, the employer proves to the satisfaction of the court that he had used due diligence to enforce the execution of this Act, and that the said other person had committed the offence in question without his knowledge, consent or connivance, the said other person shall be summarily convicted of the offence, and the employer shall be exempt from any penalty.

2. Subject to the provisions of this schedule a defendant shall be discharged from any prosecution under this Act for selling, or offering or exposing for sale reconstituted cream if he proved to the satisfaction of the court that he had purchased the article in question as cream, and with a written warranty or invoice to that effect, and that he had no reason to believe at the time of the commission of the alleged offence that the article was not cream and that at that time the article was in the same state as when he purchased it.

3. A warranty or invoice shall only be a defence to proceedings under this Act if—(a) the defendant has within seven days of the service of the summons sent to the prosecutor a copy of the warranty or invoice with a written notice stating that he intends to rely on it and specifying the name and address of the person from whom he received it and has also sent a like notice of his intention to that person; and (b) in the case of a warranty or invoice given by a person resident outside the United Kingdom the defendant proves that he had taken reasonable steps to ascertain and did in fact believe in the accuracy of the statement contained therein.

4. The person by whom the warranty or invoice is alleged to have been given shall be entitled to appear at the hearing and to give evidence, and the court may, if it thinks fit, adjourn the hearing to enable him to do so.

5. Where the defendant is a servant of the person who purchased the article under a warranty or invoice he shall be entitled to rely on the provisions of this schedule in the same way as his employer would have been entitled to do if he had been the defendant, provided that the servant further proves that he had no reason to believe that the article was not cream.

6. Every person who wilfully applies to an article in any proceedings under this Act, a warranty of invoice given in relation to any other article, shall be guilty of an offence against this Act.

7. Every person who, in respect of reconstituted cream sold by him as principal or agent, gives to the purchaser a false warranty in writing, shall be guilty of an offence against this Act, unless he proves to the satisfaction of the court that when he gave the warranty he had reason to believe that the statements or descriptions contained therein were true.

8. Where the defendant in a prosecution under this Act has been discharged under the provisions of this schedule relating to warranties, any proceedings under this schedule for giving the warranty relied on by the defendant in the prosecution, may be taken as well before a court having jurisdiction in the place where the contravention of this Act took place as before a court having jurisdiction in the place where the warranty was given.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Use of 2,6-Dichlorophenol Indophenol as a Reduction Indicator in the Examination of Foodstuffs. J. Tillmans, P. Hirsch and E. Reinshagen. (*Z. Unters. Lebensm.*, 1928, **56**, 272–292.)—The indicator, which may be obtained by coupling a solution of 5 grms. of 2,6-dichlorquinonechlorimide (the preparation of which from *p*-nitrophenol is fully described) with 8 to 12 c.c. of an alkaline 20 per cent. solution of phenol, is very stable if stored in the dark in the form of a filtered 0.01 *N* (0.29 per cent.) solution in a phosphate buffer solution of P_H 7. It changes in colour from pale red to blue with a change in P_H from 4 to 5, and appears deep blue and colourless in the presence of oxidising and reducing reagents, respectively. The potential corresponding with the second type of change was determined by titration till colourless of the 20-fold diluted, oxygen-free stock solution with 0.01 *N* ferrous sulphate solution in the presence of sodium oxalate, in an atmosphere of oxygen-free nitrogen. The amounts of iron solution added, and the corresponding colorimeter values (*f*) and potentials against a saturated calomel electrode or a platinum electrode (standardised in a 0.1 *N* solution of ferrous and ferric sulphates in 0.02 *N* sulphuric acid) were determined. The potentials at 20° C. were obtained from the formula $0.02905 \log f/(1-f)$, and

values compared with the hydrogen electrode of 255 and 233 millivolts were found at P_H 6.85 and 7.01, respectively. There is a fall in potential of 1 to 2 millivolts for a rise in temperature of 1°C . (*cf.* Hirsch and Ruter, *Z. anal. Chem.*, 1926, **69**, 217). The method was used to determine the effects of formaldehyde and varying degrees of heat on the Schardinger reaction of milk, but no definite results were obtained. The oxidation-reduction potentials of milk in the presence of 5 per cent. of mercuric chloride, however, gave an indication of these effects. Indefinite results were also obtained when the method was applied to the determination of the nature and degree of putrefaction of meat extracts (Tillmans, Hirsch and Kuhn, *ANALYST*, 1927, **52**, 289). Artificial lemon juice was distinguished from the natural product by the fact that it produced no decolorisation of the indicator. The nature of the constituents responsible for these phenomena is discussed.

J. G.

Thiocyanogen Value of Parsley Seed Oil. A. Steger and J. van Loon. (*Z. Unters. Lebensm.*, 1928, **56**, 365-367.)—The authors have applied Kaufmann's method of determining the thiocyanogen value (*ANALYST*, 1926, **51**, 157, 264) to the determination of the linolic and saturated acids in parsley seed oil. The following is the revised composition of the oil:—Unsaponifiable matter, 30; total fatty acids, 65.2 (comprising: saturated acids, 3.0; petroselinic acid, 45.0; 9, 10-oleic acid, 8.0; linolic acid, 9.1 per cent.); glycerol residue, 2.8; and volatile matter, 2.0 per cent. Petroselinic acid is an octodecene (6)-acid isomeric with oleic acid previously obtained by the authors (*Rec. trav. Chim.*, 1927, **46**, 492) from an extract of parsley seeds in petroleum spirit. Twitchell's lead salt and alcohol method cannot be used for separating the fatty acids of this oil, owing to the fact that the lead salt of petroselinic acid is fairly insoluble in cold alcohol. Bertram's oxidation method (*Z. deutsch. Oel. u. Fett. Ind.*, 1925, **45**, 733) is also not applicable.

J. G.

Castanha de Arara Nuts. A New Oil Seed from Brazil. (*Bull. Imp. Inst.*, 1928, **26**, 416-418.)—A sample of Brazilian "Castanha de arara" nuts, stated to be from *Joannesia heveoides* Ducke (Nat. O. *Euphorbiaceae*) was examined and found to agree closely both in size, proportion of shell and kernel, constants for the oil, and analysis of the residual meal with a sample of arara nuts examined in 1924. The nuts ($2-2\frac{1}{2}$ inches in length by $1\frac{1}{8}$ to $1\frac{1}{2}$ inches diam.) consisted of 55.2 per cent. of shell and 44.8 per cent. of kernel and were of an average weight of 53.8 grms. The kernels contained 4.6 per cent. of moisture, and on extraction with petroleum spirit gave 61.4 per cent. of a pale yellow liquid oil of sp. gr. at $15^\circ\text{C}/15^\circ\text{C}$., 0.9239; n_D^{20} , 1.467; saponification value, 188.5; iodine value (Hübl, 17 hours), 129.8; unsaponifiable matter, 0.48 per cent., and acid value, 2.1. A thin film of oil took 11 days to dry (*cf.* 8 days for linseed). The residual meal contained: Water, 8.0; crude proteins, 47.4; fat, 0.7; starch (by difference), 25.1; crude fibre, 6.5; and ash, 12.3 per cent. The oil could be readily used for soap making and possibly, after "boiling," for paint when in admixture

with linseed oil. Its edible use is doubtful, and since an alkaloidal substance appears to be present in the meal, physiological experiments would be necessary before the meal could be used as a cattle food.

D. G. H.

Examination of Lard in Ultra-Violet Light. F. Weiss. (*Z. Unters. Lebensm.*, 1928, **56**, 341-355.)—The behaviour of a large number of samples of lard of widely different origin in ultra-violet light has been examined, and the nature of any fluorescence or opalescence produced in each case is recorded, together with the taste, odour, and behaviour on setting of the sample. The effects of the action on the lard of activated charcoal, heat, light, air or carbon dioxide, were also studied under varying conditions. In general, the lards could be classed in 6 divisions:—(1) Lards obtained in the laboratory, and certain good commercial lards which showed either no fluorescence or yellow, white or pale blue fluorescence. (2) The same samples after exposure to air and light, when the fluorescence might be modified, *e.g.* the blue colour confined to the upper layers. (3) The same samples which, after treatment with activated charcoal, gave the same results as in (2). (4) Laboratory samples, heated to 150 to 170° C. or in superheated steam, and heated commercial lards which showed a white fluorescence with sharply defined rings. (5) Lards refined by Dutch methods which showed a characteristic clear blue fluorescence. (6) The same samples after heat or charcoal treatment, and "unrefined white grease," which showed white, blue or violet fluorescence with ring-formation decreasing in the lower layers. This classification is not rigid, since not only is the fluorescence dependent on the type of lard, but also it may be modified considerably by the drastic processes involved in refining. The conclusion of Feder and Rath (*cf.* Van Raalte, *ANALYST*, 1929, 110) that the substance causing fluorescence is present in the unsaponifiable matter, and is related to the presence of paraffin hydrocarbons, is criticised and modified, since the unsaponifiable matter of a fluorescent lard fails to produce the same degree of fluorescence when added to a non-fluorescent lard. Changes in fluorescent properties due to heat may result from oxidation of cholesterol, and ultra-violet rays themselves may play a similar part.

J. G.

Mineral Constituents of Cranberries. F. W. Morse. (*J. Biol. Chem.*, 1929, **81**, 77-79.)—Recently Morse (*J. Biol. Chem.*, 1928, **79**, 409; *ANALYST*, 1928, **53**, 659) recorded the iodine content of Cape Cod cranberries, and results are now given of determinations which were made of the mineral constituents of cranberries from the crop of 1925. Samples of the berries were weighed out, cut in halves, dried in a steam oven, cooled, weighed, ground in an iron mortar to pass through a 1 mm. mesh sieve, and bottled for analysis. Methods of the Association of Official Agricultural Chemists, Washington, 1920, were used in the determinations of the constituents, except potassium and iron. Potassium was precipitated and weighed as the perchlorate, and iron was determined in specially prepared charges of the cranberries (which had been dried without cutting, and ground in a porcelain mortar) by the colorimetric thiocyanate method after incineration and solution of the material. Analyses gave the following percentages,

calculated to the basis of fresh fruit—the figures in brackets are earlier data :—Water, 88.44 ; ash, 0.158 (0.18) ; potassium oxide, 0.068 (0.086) ; sodium oxide, 0.003 (0.012) ; calcium oxide, 0.018 (0.033) ; magnesium oxide, 0.009 (0.012) ; phosphorus pentoxide, 0.019 (0.026) ; sulphur, 0.005 ; chlorine, 0.004 ; iron, 0.00022 ; manganese, 0.00057. Lindow and Peterson (*J. Biol. Chem.*, 1927, **75**, 173, 174 ; *ANALYST*, 1928, **53**, 43–44) published data for manganese in a long list of foods, and their results on fruits show these cranberries to be comparatively high in the element. The results show that fresh cranberries generally contain less than 0.2 per cent. of total ash. The individual mineral constituents of the cranberry form very small percentages of the whole fruit. P. H. P.

Identification of Yohimbine by Microcrystallography. G. Denigès. (*Bull. Soc. Pharm. Bordeaux*, 1928, **3**, 152 ; *J. Pharm. Chim.*, 1929, **121**, 27–28.)—A small portion of the free base is treated on a slide with hydrochloric acid (1:10) and warmed until a fine ring of crystallised hydrochloride appears ; after spontaneous evaporation of the solution the crystals have a flat rhomboidal appearance under the microscope, and are isolated or in groups resembling cholesterol crystals. To liberate the alkaloid the hydrochloride is dissolved in a trace of water and very dilute ammonia added until the precipitate which forms at first is dissolved, after which heat is applied till crystallisation begins. After evaporation the yohimbine crystals appear either as long prismatic needles grouped round a centre, or more or less in the prismatic form shown by magnesium ammonium phosphate. D. G. H.

Biochemical.

Studies in Milk Secretion based on the Variations and Yields of Milk and Butter Fat produced at Morning and Evening Milkings. S. Bartlett. (*J. Agric. Sci.*, 1929, **19**, 36–47.)—Tables and curves are given which show month by month the lactation yields of cows in respect of milk and fat, morning and evening yields being treated separately and differences in relative proportions indicated. Smaller proportions of milk and of fat at the morning milkings are yielded in early lactation by all cows, but particularly by heifers and heavy-yielding cows with relatively small udders, and it is suggested that, with such animals, re-absorption of milk occurs during a long night interval.

As regards seasonal variations, November and December are the months of lowest production of milk, whilst May and June give the highest production. The morning milking does not respond as much as the evening milking to the stimulus to secretion which operates during May and June. The trouble experienced during these two months on many farms with milk of poor quality is due to : young grass ; increased secretion of milk ; the calving of a large proportion of cows during the late winter, many of these cows reaching the lactation stage when the rate of milk secretion is at its maximum and the percentage of fat at its minimum during May and June ; excessive udder pressure at the morning milking,

with resultant depression in the percentage of fat; the occurrence of occasional samples of poor quality, although the average quality may be the same as in other months.

T. H. P.

Metabolism of Laevulose, with a Colorimetric Method for its Determination in Blood and Urine. R. C. Corley. (*J. Biol. Chem.*, 1929, **81**, 81-98.)—The method of van Creveld (*Klin. Woch.*, 1927, **6**, 697) for the determination of laevulose, which had several disadvantages, including difficulty of measurement in a colorimeter, has been modified, and the new procedure has been found satisfactory in the analysis of aqueous solutions, urine and tungstic acid blood filtrates. One volume of the solution to be analysed, 0.5 volume of concentrated hydrochloric acid, and 0.1 volume of a 20 per cent. alcoholic solution of diphenylamine in a large test-tube are heated in a boiling water-bath for 15 minutes and then cooled. The tube is closed with a rubber stopper with a hole stuffed with glass wool, and the mixture may be kept indefinitely before the remainder of the determination is completed. The solution is shaken with a third of its volume of liquid (melted) phenol, which causes the immediate absorption of the diphenylamine together with the colour. The addition of 0.5 volume of 95 per cent. alcohol renders the mixture homogeneous and suitable for colorimetric comparison, which need not be made immediately. The colour slightly darkens on standing. Standards of solutions of laevulose which range downwards from 1 mgrm. of laevulose per c.c. of solution are prepared similarly and simultaneously. Recoveries of added laevulose in aqueous solution are from 97 to 103 per cent., and in blood from 95 to 105 per cent. Glucose yields about 3 per cent. of the colour of laevulose. The method is theoretically applicable to the determination of the laevulose in any substance yielding it on acid hydrolysis. Experiments on the metabolism of laevulose in the rabbit gave the following results. Laevulose appeared in the blood in small amounts after intestinal administration to rabbits. Mild poisoning with what are considered hepatotoxic agents had little influence on the laevulose present in the blood after intestinal administration. Under more rigorous conditions a certain effect has been observed in a few cases. Laevulose practically disappeared from the blood of rabbits in 90 minutes after the intravenous injection of 2 grms. per kilo of body weight. The rate of disposal of intravenously injected laevulose was little influenced by liver poisons, except with heavy doses. Laevulose injected intravenously simultaneously with insulin has been found to protect the rabbit against the latter, without there being any striking influence on the rate of removal of the circulating laevulose. If insulin has been given subcutaneously or intravenously an hour or more previous to the intravenous injection of laevulose, insulin shock has been observed on numerous occasions, and laevulose has disappeared more rapidly from the blood.

P. H. P.

Quantitative Determination of the Amide Nitrogen of Blood. S. Bliss. (*J. Biol. Chem.*, 1929, **81**, 129-135.)—On the assumption that ammonia is transported in the blood in the form of a complex that might yield ammonia again under physiological conditions, a search was made to see whether an

enzyme could be found in kidney tissue capable of liberating ammonia from a compound in blood that did not yield the ammonia by ordinary direct aeration of the blood made alkaline with sodium carbonate. Such an enzyme was found and will be described in a separate communication. Its action showed certain facts: (1) The absolute value for the "ammonia complex" of blood is many times that of the old low ammonia values. (2) The values so obtained show excellent correspondence with the physiological state (the expected variations with double nephrectomy, alkaline tide, bicarbonate feeding, etc.). (3) The "ammonia complex" of blood is completely precipitated with the proteins by the common protein precipitants. (4) The enzyme resembles a deamidase, probably a protein deamidase. (5) The absolute values obtained by acid hydrolysis of the protein fraction of blood are of the same order of magnitude as those obtained by enzymatic hydrolysis. Due to the more rapid, complete, and satisfactory hydrolysis of amides by acids, as compared with enzymes, together with the labour involved in the purification of the new protein deamidase, a method has been developed for the quantitative determination of the amide nitrogen of blood. After the tungstic acid precipitation of the proteins of blood, the precipitate is washed with tungstic acid to remove traces of urea, dissolved, and a portion of it subjected to hydrolysis with sulphuric acid at the temperature of the boiling water bath. After the neutralisation of the sulphuric acid, the mixture is aerated with an excess of sodium hydroxide, and the ammonia Nesslerised as in the standard micro-aeration method of Folin and Macallum (*J. Biol. Chem.*, 1912, 11, 523). The unavoidable error of the method is less than 1 per cent. Results by this method show that the normal level of amide nitrogen for blood drawn from the cubital vein in the human varies from 134 to 144 mgrms. of amide nitrogen per 100 c.c. of blood.

P. H. P.

Colorimetric Determination of Blood Calcium. J. H. Roe and B. S. Kahn. (*J. Biol. Chem.*, 1929, 81, 1-8.)—The colorimetric method of Roe and Kahn (*J. Biol. Chem.*, 1926, 67, 585) for the determination of blood calcium, in which the calcium is precipitated from an alkalinised trichloroacetic acid filtrate as calcium phosphate, and determined as phosphate by the method of Benedict and Theis (*J. Biol. Chem.*, 1924, 61, 63; *ANALYST*, 1924, 49, 537-8) has now been simplified and shortened, and the modification described is believed to be more accurate than any other method for the determination of blood calcium. In the new procedure the calcium phosphate is precipitated, washed, dissolved in molybdic acid, and treated for colour production in the same tube, and thus all transfers which would require time and offer chances for error are eliminated; the method of Fiske and Subbarow (*J. Biol. Chem.*, 1925, 66, 375; *ANALYST*, 1926, 51, 205-6) for the determination of inorganic phosphorus is used instead of that of Benedict and Theis, but the latter procedure is retained as an optional method where a reducing agent of greater keeping qualities is desired (according to Fiske and Subbarow their amino-naphtholsulphonic acid reagent will keep for 2 weeks, but the authors find it quite satisfactory if freshly prepared every 2 or 3 months); a more successful washing mixture, namely, 55 parts of ethyl alcohol, 10 parts of

amyl alcohol, and 35 parts of water, made just alkaline to phenolphthalein, has been developed for the calcium phosphate precipitates, which eliminates the second washing; the calcium is precipitated at a higher alkalinity to remove any possibility of interference by unusual amounts of magnesium; and a number of minor changes in technique are also introduced. This method is not dependent upon a balancing of compensating errors, and by it very small amounts of calcium (0.02 mgrm.) can be determined. It is stated that colorimetry is the logical procedure for the determination of blood calcium, since calcium is present in the blood in relatively small amounts. The micro method for blood calcium of Kuttner and Cohen (*J. Biol. Chem.*, 1927, **75**, 517), adapted from the original method of the authors, is criticised on the grounds that it does not provide for the possibility of interference by unusual amounts of magnesium, that the stannous chloride reagent recommended is not specific for phosphomolybdic acid, and that with this reagent the non-changing zone of colour production is so exceedingly small (between 0.02 and 0.022 per cent.). The authors are engaged in the application of their method to the development of a micro method. P. H. P.

Action of Cholesterol from Cod-Liver Oil on a Photographic Plate. L. Hugounenq and E. Couture. (*Compt. rend.*, 1929, **188**, No. 4, 349-350.)—In the course of a comparative study of cholesterol of different origins, it has been found possible to distinguish the cholesterol from cod-liver oil from cholesterol from other sources. Cholesterol from sources such as gallstones, or ox brain, spread on a photographic plate and left for several days, has no effect on the plate, whereas, on development of a plate which has had crystals of cholesterol from cod-liver oil on it under similar conditions, very definite black stains appear wherever the crystals have been in contact. An experiment showed that cholesterol from cod-liver oil placed on a thin quartz plate and left for six days in absolute darkness affected a photographic plate on which the quartz plate was lying, whilst the use of a similar glass plate (in the place of the quartz) gave negative results. Therefore the action appears to be a physical one, and further study of this subject is being carried out. P. H. P.

Antirachitic Properties of Cod-liver Meals. R. M. Bethke, G. Zinzalian, D. C. Kennard, and H. L. Sassaman. (*J. Agric. Res.*, 1928, **36**, 747-753.)—In recent years, the residue left after the production of cod-liver oil from the livers of the codfish (*Gadus callarias*) has been dried and sold in the open market under the name "cod-liver meal." It has been claimed that this liver residue, apart from the quality of its proteins, has certain vitamin properties, principally those of an antirachitic nature; thus its nutritional value is of great interest. Cod-liver oils may vary greatly in their vitamin A and D content, and, likewise, the residue which remains after the partial extraction of the fats would be expected to vary in vitamin properties, depending upon the original vitamin content of the livers, the amount of oil remaining in the residue, the method employed for the oil extraction, and the procedure used in drying the liver residue. Experiments

on their antirachitic properties have been carried out on three cod-liver meals obtained from three different manufacturers after the removal of the oil by the steam process. Experiments with chicks and rats have shown conclusively that these dried residues which remain after the extraction of oil from fresh cod livers vary markedly in their antirachitic properties. The antirachitic variation was not proportional to the residual fat content of the livers, and the ether-extractable fraction did not prove nearly as potent as ordinary cod-liver oil. The cod-liver oil used was at least 6 times as potent antirachitically as the extract from the most efficient of the three liver meals. Therefore, it would seem unwise to use the liver meal as an antirachitic substitute for a good grade of cod-liver oil in either poultry or livestock production. It remains to be determined whether cod-liver meals may possess other merits apart from their questionable fat-soluble vitamin content.

P. H. P.

Comparison of the Antirachitic Potency of Ergosterol irradiated by Ultra-Violet Light and by Exposure to Cathode Rays. A. Knudson and C. N. Moore. (*J. Biol. Chem.*, 1929, 81, 49-64.)—It has previously been shown that antirachitic properties can be induced in various substances, such as cholesterol, yeast, etc., by exposure to high voltage cathode rays. Experiments by Rosenheim and Webster (*Lancet*, 1927, 1, 306; *Biochem. J.*, 1927, 21, 389; *ANALYST*, 1927, 52, 424) and Hess and Windaus (*Proc. Soc. Exp. Biol. and Med.*, 1927, 24, 461) have indicated that ergosterol, when irradiated by ultra-violet light, is converted into a powerfully antirachitic substance, so that as small a dose as 0.0001 mgrm. of irradiated ergosterol per day cures or prevents rickets in rats kept on a rachitogenic diet. Experiments have therefore been carried out on the antirachitic activity of ergosterol produced by exposure to cathode rays, in order to determine the best procedure for obtaining the most potent product, and to compare this potency with that obtained by ultra-violet irradiation. Rats were used for the tests. Results show that ergosterol exposed to cathode rays with the tube operating at 180,000 to 200,000 volts is not rendered as potent as when irradiated with ultra-violet light from a mercury vapour quartz lamp. The highest potency obtained by cathode ray exposure (*i.e.* the lowest dose obtained which brings about a healing effect of rickets) was 0.0005 mgrm. per day, and by ultra-violet irradiation the highest potency was 0.00002 mgrm. per day. Ergosterol exposed to ultra-violet light for 15 seconds was more potent than that exposed for 30 minutes, although 30 minutes has been the time more or less generally used by a number of investigators. Ergosterol exposed to cathode rays undergoes a similar change in the absorption spectrum as when exposed to ultra-violet light. A plate which shows the absorption spectra is reproduced. The manner in which cathode rays produce their antirachitic action does not seem to be due to the production of ultra-violet light, for yeast, cholesterol and ergosterol were not activated when exposed to cathode rays behind a quartz plate.

P. H. P.

Bacteriological.

Isolation of *B. paratyphosus B* from Sewage. J. D. A. Gray. (*Brit. Med. J.*, 1929, 142).—*B. paratyphosus B* (Schottmüller) was found in one of four main sewers of Edinburgh and traced to three of its seven tributary sewers. The methods tried for isolating and identifying the organism were: (1) Wilson and Blair's method—medium containing glucose, with bismuth, sulphite, iron and brilliant green (termed medium B); (2) Browning, Gilmour and Mackie's method, 1913—brilliant green enrichment method; (3) Rakieta and Rettker's modification of No. 2; (4) MacConkey's medium; (5) Wilson and Blair's medium, containing lactose, bile, salt, and brilliant green.

Any one of these methods may fail to detect paratyphoid bacilli isolated by the others. Method No. 1 has the advantage that it is a direct plating method and inhibits the growth of a very large number of coli-form organisms. The enrichment methods have the disadvantage that they tend to permit overgrowth of *B. fluorescens* and *B. proteus* types. Laboratory strains of various types were plated out on medium B. in order to obtain typical colonies, viz. *B. typhosus*, *B. paratyphosus A*, *B. paratyphosus B*, a typical *B. coli*, *B. proteus*, and *B. fluorescens*. *B. paratyphosus B* produced colonies with the following characteristics:—After 24 hours they were each 1 mm. in diameter; after 48 hours they became bright green, one of the strains producing black colonies with a metallic lustre; after four day's incubation the colonies were 6 mm. in diameter and had a raised greyish centre. None of the other varieties of organisms behaved in this way; for instance, *B. typhosus* and *B. paratyphosus A* produced only minute colonies. For confirmation of *B. paratyphosus B* sub-inoculations were carried out on Wilson's modification of the Endo medium, in which sucrose is used instead of lactose. Samples from those sewers giving positive results by method No. 1 on arrival at the laboratory were again tested after one, two, and four days, with negative results, thus indicating that *B. paratyphosus B* has a very short period of survival. Loss of motility in laboratory strains of *B. paratyphosus B* was observed when plated on medium B, but this property returned after the organism was sub-inoculated into ordinary nutrient media. It is pointed out that the district from which the sewers came, in which *B. paratyphosus B* was found, was the locus of an outbreak of paratyphoid B fever in 1927, probably caused by the flooding of byres due to the main sewer being unable to cope with flood water. Milk obtained in these byres probably became infected. The Medical Officer considered that the infection originated in resident "carriers" rather than in the numerous piggeries in that district.

R. F. I.

Agricultural.

Rapid Electrometric Method for Measuring "Lime Requirements" of Soils. F. Hardy and A. H. Lewis. (*J. Agric. Sci.*, 1929, 19, 17–25.)—The Hutchinson and MacLennan method for determining the lime requirement of a soil, depending on the interaction between calcium bicarbonate in aqueous solution

and the components of acid soils, is tedious and slow, and gives reproducible results only when the experimental conditions are strictly standardised. Moreover, the concentration of calcium bicarbonate recommended, namely, 0.02 *N*, is such that the solution is initially acidic (P_H 6.2), and may become more acidic (*e.g.* P_H 5.5) when finally in equilibrium with an acid soil. Again, although the concentration of calcium ion in the solution is relatively high, it is certainly not high enough to effect complete replacement of hydrogen ion from the soil adsorption complex, so that this method does not fully reproduce the various effects caused by liming a soil in the field.

In the method devised by the authors, 10 grms. of the air-dry soil, previously passed through a 1 mm. sieve, are mixed with 40 c.c. of neutral 0.2 *M* calcium chloride solution by shaking in a 150 c.c. wide-mouthed, hard glass bottle. Except with soils containing traces of free lime, no lengthy period of contact of soil and solution is necessary. A sufficient quantity of quinhydrone is then added to the mixture and the P_H value determined by the quinhydrone electrode. The mixture is next titrated with 0.03 *N* lime water in successive portions of 5 c.c., the liquid being shaken for three minutes, and the P_H determined, after each addition. This procedure is continued until the reaction has passed P_H 7.0, the results being plotted and the exact volume of the lime water needed to give the final reaction P_H 7.0 determined from the graph. This method gives results which are reproducible with any given salt-treated soil, and are much more regular than, and, in accordance with expectation, usually greater than those furnished by the Hutchinson and MacLennan method. Thus, it brings out clearly the proportionate increase in lime requirements (*a*) of soils of approximately the same initial exchange reaction but of increasing fineness of texture, and (*b*) of soils of approximately the same texture, but of increasing exchange P_H value. The results given by this electrometric method are compared with those yielded by a base-exchange method, the latter being appreciably the higher.

T. H. P.

Organic Analysis.

Determination of Iodine (Halogen) in Organic Matter. J. Schwaibold. (*Chem. Ztg.*, 1929, 53, 22-23.)—In the determination of iodine in organic materials, the inconveniences involved in the incineration in an open vessel in presence of a large amount of alkali, particularly the difficulty of preventing of loss of halogen during complete combustion of carbon, may be obviated by a procedure similar to the combustion method of determining carbon and hydrogen. Use is made of a hard (Supremax) glass combustion tube, 90 cm. long and 20 to 30 mm. wide, in which is placed a porcelain or nickel boat containing the dry substance, liquids being previously dried, preferably in the boat itself, after being rendered slightly alkaline. Platinum contact material is placed between the boat and the drawn-out end of the combustion tube, which is connected, by glass-to-glass joints, with two efficient wash-bottles, preferably of the Greiner and Friedrichs type, charged with 20 and 10 drops

respectively of saturated potassium carbonate solution. After the tube has been filled with oxygen purified by passage through concentrated potassium hydroxide solution and soda-lime, the platinum contact material is heated to redness and the substance itself then gradually heated, the heating and the oxygen current being continued until the organic matter is completely burned and no vapours or fumes are visible at the end of the tube. The wash bottles and the tube are washed out and the boat boiled in water, the residual material being tested, in the case of an unknown substance, to ensure its freedom from iodine. The total liquid is evaporated and, when most of the water has been expelled, filtered. If the amount of iodine is large, an aliquot part of the solution is titrated by Winkler's method, but with small amounts of iodine, the still aqueous residue left on evaporation is extracted with alcohol and the determination by Winkler's method carried out after expulsion of the alcohol by distillation. Sometimes, when large amounts of substance are used, white fumes reach the receiver, especially during the early stages of the combustion, owing to incomplete combustion. In such a case, the resulting liquids are evaporated in a platinum dish and the residue heated over a small flame until quite white; the subsequent treatment is then as usual. With thyroid gland, milk, urine, and moorland soil, the method gives satisfactory results.

T. H. P.

Qualitative Colour Test for Reactive Organo-Metallic Compounds.

H. Gilman and L. L. Heck. (*Rec. Trav. Chim. Pays-Bas*, 1929, **48**, 193-197.)—Modifications of this test (*ANALYST*, 1925, **50**, 523), in which test papers, a spot plate, or one drop of solution in a test-tube are used, prove unsatisfactory as regards sensitiveness, and the original method, in which 1 c.c. of solution is employed, is preferred. The results obtained with a number of typical Grignard reagents show that the sensitiveness of the test is increased by using a hot, saturated solution of the Michler's ketone in benzene, the coloration then appearing immediately. If cold solutions are used, positive results are obtained if the liquid is allowed to stand for 3 to 4 minutes prior to hydrolysis. For various Grignard reagents the minimal quantities necessary for the test are given.

T. H. P.

Specific Gravity of Glycerol. **L. W. Bosart and A. O. Snoddy.** (*Ind. Eng. Chem.*, 1928, **20**, 1377-1379.)—Since the publication of the authors' tables for the specific gravity of glycerol (*ANALYST*, 1927, **52**, 434), the third volume of the International Critical Tables has been published, and it contains tables showing the absolute density of glycerol at various temperatures. The figures in the two tables are in fair agreement, except those given for the specific gravities at 20° C. While disclaiming any desire to criticise the work of the compilers of the International Critical Tables, the authors consider that these tables are unsatisfactory as a working basis where accuracy in the fourth decimal place is necessary.

W. P. S.

Film Characteristics of the Esters of the Component Fatty Acids of Linseed Oil. **B. H. Thurman and W. R. Crandall.** (*Ind. Eng. Chem.*, 1928, **20**, 1390-1392.)—Experiments with mixtures of ethyl esters of linseed oil fatty

acids with a nitrocellulose lacquer showed that the esters of the less unsaturated fatty acids (oleic acid type) are very stable in films, whilst those of the more unsaturated fatty acids are not so stable, as is shown by their rapid tendency to become sticky, odorous, and dark coloured. The difference in the darkening in colour of certain of the films, as compared with others, indicates that the yellowing of drying-oil films is the result, and a necessary result, of oxidation of the highly unsaturated fatty acid groups, and that it and the drying of linseed oil films are not interdependent; it is also independent of the presence of glycerol. In the case of films containing ethyl oleate and ethyl stearate, the latter tended to crystallise on the surface when the film was cooled below 35° C. W. P. S.

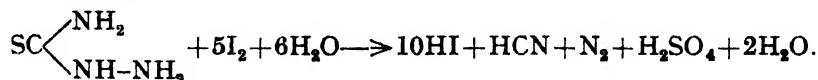
Composition of German Rape Oil. K. Täufel and C. Bauschinger. (*Z. Unters. Lebensm.*, 1928, **56**, 253–264.)—The oil was obtained by extraction under pressure (yield 21 per cent.), and was filtered at 40° C., purified by treatment with sulphuric acid, washed acid-free and dried. A list of its properties and constants is given. The total fatty acids were then separated from the oil, dissolved in 95 per cent. alcohol, and precipitated with suitable quantities of lead acetate solution (Twitchell, *ANALYST*, 1921, **46**, 466), and the precipitate filtered off after 12 hours at 15° C., washed with alcohol and recrystallised from ether. The operation was repeated three times, and the fatty acids obtained then dissolved in alcohol and fractionally precipitated six times with a 1 per cent. solution of lithium acetate in 95 per cent. alcohol. The purity of the product was controlled by iodine value, m.pt. and molecular weight determinations, and the original precipitate was shown to contain 18.85 per cent. of saturated fatty acids and 81.15 per cent. of erucic acid. The filtrate from the Twitchell separation was treated with an alcoholic solution of magnesium acetate, and erucic acid (23.45 per cent. of the total fatty acids) liberated from the magnesium salt obtained and recrystallised from alcohol. The mother-liquor, which contained a little erucic acid, all the oleic acid and the higher unsaturated fatty acids, was brominated at –14° C. for 3 hours, the bromide filtered off, washed with cold ether and weighed. The amount of α -hexabromstearic acid (m.pt. 179° C.) was found to correspond with 2.45 per cent. of linolenic acid. The residue left on evaporation of the mother liquor was warmed at 35° C. with petroleum spirit for 20 minutes, and an amount of α -tetrabromstearic acid (m.pt. 114° C.) corresponding with 5.42 per cent. of α -linolic acid was obtained. This separation depends on the fact that the hexabromide is sparingly soluble in ether or petroleum spirit, whilst the tetrabromide is readily soluble only in ether. The oleic acid was determined by precipitation of an alcoholic solution of the fatty acids with zinc acetate solution (Grabner, *Monatsh.*, 1921, **42**, 287). The percentage composition of the oil was therefore:—Saturated fatty acids, 0.8; erucic acid, 43.5; oleic acid, 37.8; linolic acid, 10.6; linolenic acid, 3.5; unsaponifiable matter, 1.0; and glycerol residue (as C_3H_2) 3.8 (*cf.* following abstract). J. G.

Glycerides of Rape Oil. K. Täufel and C. Bauschinger. (*Z. Unters. Lebensm.*, 1928, **56**, 265–272.)—The presence of oleo-linolen-erucin, oleo-dierucin,

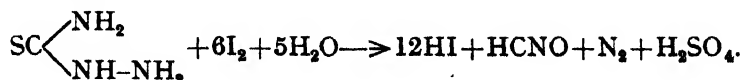
and trierucin in rape oil has been established (*cf.* Amberger, *id.*, 1920, 40, 192). The amounts of oleo-dierucin and trierucin are uncertain, and cannot be obtained from the erucic acid content, on account of the presence of other mixed glycerides containing this acid. Molecular weight and bromine determinations on the products resulting from fractional crystallisation of the brominated glycerides indicated 1.7 per cent. of oleo-linolen-erucin, corresponding with 0.5 per cent. of linolenic acid, and it is concluded that the remainder of the acid is combined in a different form (*cf.* preceding abstract). Fractional crystallisation from acetone at 20° C. and 0° C. of the elaidin produced by the method of Tomow (*viz.* by the action of gaseous nitrous acid on a mixture of equal parts of oil and acetone at ordinary temperatures; see also Heiduschka and Felser, *Z. Unters. Lebensm.*, 1919, 38, 241), gave elaido-dibrassidin ($C_3H_5(C_{22}H_{41}O_2)_2(C_{18}H_{33}O_2)$) and tribrassidin ($C_3H_5(C_{22}H_{41}O_2)_3$). J. G.

Determination of Fat in Leather. D. Woodroffe. (*J. Inter. Soc. Leather Trades' Chem.*, 1928, 12, 569).—In a previous paper (*id.*, 1926, 219) the author found that leathers which had been dried gave a lower figure for fat content, as found by a Soxhlet extraction, than if they had not been dried, but that if the dried leather were allowed to remain in a moist atmosphere for some days, the fat content became higher, approximating to the original figure. The explanation given in the present paper is that petroleum spirit extracts of air-dry leathers (containing 17 to 20 per cent. of moisture) persistently retain small amounts of moisture when dried in a water-oven for periods up to 16 hours. If heated for 3 hours at 105° C., the water appears to be driven off and a more accurate result is obtained, but there is danger of decomposing triglycerides. The author recommends the use of the vacuum oven for the purpose. R. F. I.

Determination of Thio-semi-carbazide by means of Iodine. A. Gaffre. (*J. Pharm. Chim.*, 1929, 121, 19–23).—In an iodimetric determination thio-semi-carbazide reacts like its two associated components—thiocyanic acid and hydrazine. In the presence of sodium carbonate, and with at least 8 hours of contact with the iodine, cyanogen iodide is formed, and then is decomposed on the addition of acid, with liberation of 2 atoms of iodine. The acid is added before titrating the excess of iodine; 10 atoms of iodine are taken by 1 molecule of thio-semi-carbazide.



In the presence of sodium hydroxide, with at least 30 minutes' contact, and on titration of the excess of iodine after acidification, 12 atoms of iodine are consumed by 1 molecule of thio-semi-carbazide.



D. G. H.

Decomposition of Phenolsulphonic Acids and Purification of Phenols by the Sulphonic Acid Separation Method. H. Bruckner. (*Z. anal. Chem.*, 1928, 75, 289-292.)—The sulphonic acids corresponding with various phenols are decomposed by steam at the following temperatures, which are independent of the concentration either of the sulphonic acid or of the sulphuric acid: 1-hydroxybenzene-4-sulphonic acid, 123-125° C.; 1-methyl-2-hydroxybenzene-5-sulphonic acid, 133-135° C.; 1-methyl-3-hydroxybenzene-6-sulphonic acid, 116-119° C.; 1-methyl-4-hydroxybenzene-3-sulphonic acid, 133-136° C.; 1:2-dimethyl-3-hydroxybenzene-6-sulphonic acid, 115-118° C.; 1:2-dimethyl-4-hydroxybenzene-5-sulphonic acid, 107-111° C.; 1:3-dimethyl-2-hydroxybenzene-5-sulphonic acid, 124-128° C.; 1:3-dimethyl-4-hydroxybenzene-5-sulphonic acid, 121-125° C.; 1:3-dimethyl-5-hydroxybenzene forms no sulphonic acid with concentrated sulphuric acid and can be distilled over by steam at 100° C.; 1:4-dimethyl-2-hydroxybenzene-5-sulphonic acid, 115-118° C.

These varying temperatures may be utilised for the purification of phenols. The sulphonation is best effected by heating the phenol gently with an equal weight of concentrated sulphuric acid and stirring with a glass rod until no stream lines remain visible, and then heating the mixture for 3 hours in an oven at 103-105° C. The mass is diluted with 200-300 c.c. of water and steam is passed through the boiling solution until all non-sulphonated phenol is expelled. The cold liquid is shaken with ether, which extracts resinous products, the pure sulphonic acid being obtained by evaporating the residual liquor at a rather higher temperature and, finally, by drying over sulphuric acid or phosphorus pentoxide. To prepare pure *m*-cresol from the commercial product, this is sulphonated and freed from non-sulphonated ingredients as above. The solution is then evaporated on an air-bath or in an oil-bath and with a gentle current of steam passing through it until the boiling point reaches the decomposition temperature (117-118° C.), which is maintained for some time by gentle heating and a vigorous current of steam. The *m*-cresol is thus distilled and separates in the condensate as an oil, which is purified by extraction with ether and distillation. A yield of about 80 per cent. of pure *m*-cresol is thus obtained from a 97-98 per cent. pure product.

T. H. P.

Inorganic Analysis.

New Method for the Quantitative Determination of Ozone in Air. M. S. Egorow. (*Z. Unters. Lebensm.*, 1928, 56, 355-364.)—The method for the determination of small quantities of ozone in which the iodine liberated from potassium iodide is titrated with sodium thiosulphate solution is not sufficiently sensitive. The fluorescein method of Benoist (*ANALYST*, 1919, 44, 183) has the disadvantage that the reaction is slow, and the ozone is destroyed, and the author suggests instead the formation of fluorescein from its non-fluorescent leuco-compound (fluorescin), by the action of ozone. Fluorescein (1 mgrm.) is dissolved in a few drops of 10 per cent. sodium hydroxide solution, 10 c.c. of a saturated solution of sodium hydroxide added, and the mixture shaken

with zinc dust, and filtered when the disappearance of fluorescence indicates that reduction is complete. One drop of freshly made solution is placed in a test-tube with 10 c.c. of 0.5 per cent. sodium hydroxide solution, and the ozonised air drawn through the liquid at a maximum rate of about 12 to 15 litres per hour by means of a graduated water-aspirator. If the tube is placed in an illuminated comparator, the flow may be stopped, and the volume of air measured when the fluorescence matches that of a standard solution containing 1 part of fluorescein in 100,000,000. The fluorescence is stable in alkaline solutions and is unaffected by hydrogen peroxide or oxides of nitrogen, and the method is sensitive, rapid and specific. One part by weight of fluorescein is produced by 0.96 part of ozone.

J. G.

Determination of Cadmium in Organic and Inorganic Compounds. H. ter Meulen and (Mlle) H. J. Ravenswaay. (*Rec. Trav. Chim. Pays-Bas*, 1929, 48, 198-200.)—Cadmium may be determined in the same way as arsenic (*ANALYST*, 1926, 51, 421), except that no spiral of platinum foil is required. If the substance contains sulphur or a halogen, it is mixed in the boat with calcium carbonate. To prevent traces of unreduced cadmium halide from reaching the incandescent zone of the tube, the hydrogen is passed through a wash-bottle containing concentrated ammonia solution, and then dried by means of quicklime before passing into the tube. This procedure is of advantage even in absence of halogen or sulphur. Any small quantity of ammonium halide deposited in the receiver may be removed by washing with water and then with alcohol, the deposit being dried in a current of dry air before being weighed. The cadmium in inorganic compounds and in cadmium alloys containing no other volatile metal may be determined similarly.

Attempts to determine zinc by the same method have failed, slightly high results being always obtained, owing to the formation of a film of the oxide.

T. H. P.

Ceric Sulphate as a Volumetric Oxidising Agent. VIII. Determination of Chromium. H. H. Willard and P. Young. (*J. Amer. Chem. Soc.*, 1929, 51, 139-149.)—A method is described in which the chromic salt is oxidised with ceric sulphate, the excess of which is measured potentiometrically with sodium nitrite or oxalate; or the excess of ceric salt is destroyed with sodium nitrite, the latter in turn by urea, and the chromic acid titrated with ferrous salt. Reference should be made to the original paper. (*Cf. ANALYST*, 1928, 404, 674.) W. R. S.

Fineness and Available Lime Content of Quicklimes. J. S. Rogers. (*Ind. Eng. Chem.*, 1928, 20, 1355-1356.)—Many industries prefer to use quicklime in place of slaked lime for neutralisation and other purposes, in order to utilise the heat of hydration. A properly burned lime will usually yield a slaked lime in such a fine state of division that it will pass a 200-mesh sieve; particles coarser than this consist of unburned stone, over-burned lime, impurities, etc., and are of little, if any, use. To determine fineness, 100 grms. of the sample of quicklime are added to 500 grms. of water, the mixture is agitated for five minutes and

occasionally (about six times) during the succeeding twenty-four hours, care being taken to avoid mechanical disintegration. The mixture is poured into the top sieve of a series nested in the following order :—30-mesh, 50-mesh, 100-mesh, and 200-mesh. The sieves are washed with a stream of water, dried at 110°C. , and their contents weighed. Available lime is determined by mixing 1.4 gm. of the sample with 200 c.c. of hot water, boiling the mixture for three minutes and titrating it with *N* hydrochloric acid, phenolphthalein being used as indicator ; the titration is continued until the mixture remains colourless for one or two seconds. Another portion of 1.4 grms. of the sample is then placed in a litre flask, 200 c.c. of hot water are added, the flask is closed with a cork carrying a capillary vent, the mixture boiled for three minutes, cooled, *N* hydrochloric acid added in quantity 5 c.c. less than was required for the preliminary titration, and the whole is diluted to 1 litre, shaken for five minutes, and allowed to settle. Two hundred c.c. of the clear liquid are then drawn off and titrated with 0.5 *N* hydrochloric acid. The percentage of calcium oxide is calculated from the quantity of acid used for the neutralisation. The difference between the available lime, as thus determined, and the total calcium oxide in the sample may be taken as an index of the degree to which the lime has been burned, assuming that the hydrochloric acid neutralised only the calcium hydroxide and not the magnesium hydroxide, magnesium oxide and calcium oxide.

W. P. S.

Erratum.

Rapid Method for the Determination of Selenium.—In line 5 of the abstract on p. 63 of the January issue, *for* " sodium sulphate " *read* " sodium sulphide."

Physical Methods, Apparatus, etc.

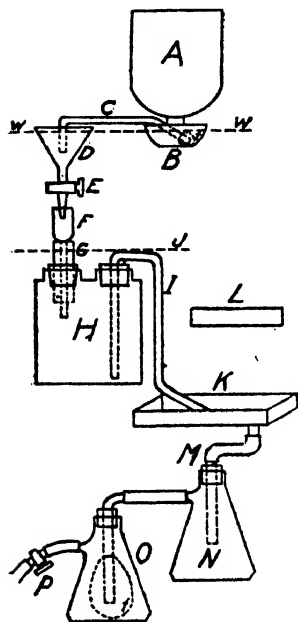
Transmission of Ultra-Violet Light through Tracing Cloth. C. H. Young. (*Nature*, 1929, 123, 47.)—Ultra-violet light passes through ordinary commercial tracing cloth (or linen) to a surprisingly large extent.

No.	Type of screen.	Approximate thickness. mm.	Mesh count per cm.	U.-V. limit in Ångström units.
	None	—	—	2225
A	Excelsior	0.070	44 × 44	2535 (faint)
B	Imperial	0.070	47 × 47	2535
C	Excelsior	0.083	47 × 47	2535 (faint)
D	Imperial	0.081	43 × 43	2482
E	Lion	0.080	41 × 41	2482
P	Newspaper	0.070	—	3984
Q	Kraft paper	0.101	—	4339 (faint)
R	Wrapping paper	0.077	—	3125
S	Writing paper	0.069	—	3125

It was found that sun-heat or heat from a red-hot ball passed through the tracing cloth to a much less extent than through glass or vita-glass, so that it is possible to screen off much of the heat and yet retain most of the ultra-violet light.

D. G. H.

Accelerated Exposure Test for Varnishes and Lacquers. H. V. Hansen. (*Ind. Eng. Chem.*, 1928, 20, 1384–1385.)—The test panels are subjected to the action of ultra-violet light while they are in alternate wet and dry conditions. The apparatus used is shown in the illustration (not drawn to scale).



The 4-litre bottle A is filled with water and inverted over the basin B so as to yield a constant water level, W. A siphon C conducts the water to the funnel D; the tap g regulates the flow of the water at any desired rate into the funnel F and thence into the 300 c.c. bottle H. A piece of muslin, f, is tied over the end of C, and the funnel D contains a filter paper, these arrangements being necessary to remove traces of dust which may settle in the basin B. On reaching the level J, the water siphons over into the tray K, containing the test panels, and situated under the carefully shielded lamp L. The water is discharged through M into the flask N, and then into a similar flask O, the inlet pipe to the latter being also fitted with a muslin filter, f, to remove particles of dust which would otherwise clog the tap P. The tap E should deliver about 60 drops per minute, the bottle H should empty into K in about two minutes, and the tap P is so adjusted that the tray K empties in fifteen minutes. There should be a fall of about 0.5 metre between K

and N. A cycle of ninety minutes wet and thirty minutes dry for the test panel is then attained. A period of twenty-four hours in the apparatus corresponds roughly to about two weeks of outside summer exposure. The test panels should be examined periodically for the first signs of cracking, blistering, or other indication of failure.

W. P. S.

Reviews.

PRINCIPLES AND APPLICATIONS OF ELECTROCHEMISTRY. In two volumes. Vol. I. **PRINCIPLES.** By H. JERMAIN CREIGHTON. Second edition, revised and enlarged. Pp. xvi+488. New York: Wiley & Sons; London: Chapman & Hall. 1928. Price 20s. net.

In view of the importance of the subject, the number of books on electro-chemistry, good and indifferent, is small. Prof. Creighton's book belongs decidedly

to the first category. It is clearly and accurately written, and gives not only an excellent review of the subject suitable for the student, but also a large amount of detail, in the form of tables, curves, literature references and descriptions of experimental methods, which makes it a valuable work of reference to the analytical chemist who has occasion to use electrical methods, the application and importance of which has increased very considerably during the last few years.

In this connection the detailed and critical descriptions of the accurate measurement of current by coulometers, of conductivity measurements, and of potentiometric titrations may be mentioned. In some cases, as in the description of conductimetric titrations and the determination of hydrogen ion concentrations, the descriptions of the methods are rather brief, and these will no doubt be dealt with more fully in the second volume. In all cases, however, a clear statement of the theory of the methods is given.

The Activity Theory and the Debye-Hückel theory of strong electrolytes are explained in sufficient detail, and here, as throughout the book, the mathematics is kept as simple as possible, and can be followed with an elementary knowledge of the calculus. Even without this, the results are so clearly stated that the reader will have no difficulty in following the use of the formulae. There is a good chapter on the theory of indicators.

The book may be recommended as an intelligible and practical account of the subject.

J. R. PARTINGTON.

PHOTOMETRIC CHEMICAL ANALYSIS. Vol. I. COLORIMETRY, by JOHN H. YOE, Ph.D. Pp. xxi+771. London: Chapman & Hall, Ltd. Price £2 2s. 6d. net.

"The rapid growth of colorimetry and nephelometry has created a demand for a comprehensive reference work on these two methods of chemical analysis. . . . During the past twenty-five years many new colorimetric methods have been developed, so that now most of the more common elements, a number of the less common ones, and many organic compounds may be determined by means of the colorimeter. The literature numbers several thousand references. Nephelometry," which is to be dealt with in Volume II, "on the other hand, is a comparatively new science. It had its beginning in the nineties when Richards used it as a means of making corrections in certain atomic-weight determinations."

This work appears to be the first to deal with these subjects so comprehensively. The author, who is a professor of chemistry in the University of Virginia, has certainly done justice to his theme, especially from the practical point of view of the analyst and the works chemist. There is little of theoretical interest, although avenues to this aspect of the subject are opened by references to instruments and literature. This is not to be regretted, since frequent correlation of practice with theory would repel the average reader of a book having as its chief aim the introduction of quick and convenient methods. However, those

who wish to explore this field will find suggestions in the references to spectroscopy and in the copious bibliography.

The book is divided into four parts. The first deals with general principles, instruments and apparatus, calculation of results, errors, and very full directions for using a precision colorimeter.

Part II comprises twenty-eight chapters covering nearly 300 pages, each chapter being devoted to a study of the methods for determining a single element, except in five cases. The general scheme may be illustrated by the chapter on Aluminium, which occupies fourteen pages. (a) Determination of Aluminium by "Aluminon":—The principles of the test are defined; then follows a list of the ten necessary reagents with directions for preparing the special ones; "Procedure" fills a page and a quarter, and three pages of "Notes" dealing with questions of sensitivity, "snags," influence of other elements, etc. (b) Determination of aluminium in non-ferrous material by "Aluminon." The general treatment is similar to that of (a); under "Procedure" three "Methods" are given. (c) Determination of aluminium by Alizarin-S, receives adequate attention, although in less than two pages. (d) Determination of aluminium by haematoxylin is dealt with in similar manner. Little is left for the average reader to discover.

Part III surveys "Organic" and Part IV "Biological" materials. The treatment is similar to that already described, but generally not nearly so full.

The volume closes with a descriptive Bibliography occupying 84 pages. The references are classified under the respective subjects. For example, 26 under aldehyde, 19 under bismuth, 128 under iron, all with some notes revealing the scope or main practical theme of the paper. It would be an improvement if, in the second edition, which one may confidently anticipate, the bibliography were divided into two sections: (a) Those papers dealing with Colorimetry generally, and (b) those concerned with single substances. At present it is easy to miss the papers of wider interest classified under "Errors" "Sensitiveness," etc.

S. JUDD LEWIS.

VOLUMETRIC ANALYSIS. Vol. I. THEORETICAL PRINCIPLES OF VOLUMETRIC ANALYSIS. By I. M. KOLTHOFF, in collaboration with H. MENZEL. Authorised translation from the German by N. H. FURMAN. Pp. 289. London: Chapman & Hall. Price 15s.

The German original of this book has established itself as a standard work; the present translation appears to follow it very closely; in some places, in fact, so closely as to prejudice the English style. The translator could easily have improved on such expressions as "the reaction runs slowly," "you will perceive a precipitate," and "if you add a little potassium permanganate." On page 135 the phrase "Yet they are responsible for many kinds of errors," appears as a complete sentence. One of the chief deficiencies of the German edition is the absence of an index; this has been made good in the translation by the addition of both author and subject indexes.

S. GLASSTONE.

FIXATION OF ATMOSPHERIC NITROGEN. By FRANK A. ERNST. Fixed Nitrogen Research Laboratory, U.S. Dept. Agric. Industrial Chemical Monographs. Pp. 154. London: Chapman & Hall. Price 12s. 6d.

In this volume a brief description is given of the three principal methods employed for the fixation of atmospheric nitrogen, the arc, the cyanamide and the ammonia processes, respectively, together with an account of the bye-products of ammonia, a review of the world-trade in nitrogen, and a bibliography of the more important articles on this subject.

In his foreword the author states that the book is not intended for the scientist or technician, but for the teacher and student, for the business man and banker.

Efforts of this kind are to be welcomed not only for the purpose of popularising science but also of drawing the attention of the man in the street to scientific facts which play an unsuspectedly important part in his economic life. One is inclined to think that the style of the volume errs a little on the technical side, for it ever to qualify as a "best seller," but it is written clearly and with vigour, it is well printed, and contains excellent diagrams. Statistics are somewhat elusive entities, and the present position of Great Britain with regard to fixed nitrogen is somewhat more satisfactory than the author would lead us to believe.

ERIC K. RIDEAL.

CREATINE AND CREATININE. By ANDREW HUNTER, M.A., M.B., F.R.S.Can., Professor of Biochemistry in the University of Toronto. Pp. vi+281. Monographs on Biochemistry. London: Longmans Green & Co., Ltd. 1928. Price 14s.

Creatine was discovered by Chevreul in meat extract in 1832, but it was only in 1904, after Folin had elaborated a quantitative method for the estimation of this substance that its importance became evident. This is particularly shown in the excellently written chapter (VIII) of the book under review, which goes to show the importance of creatinuria during growth, in women (during and after pregnancy), in starvation, in fasting, during carbohydrate privation, acidosis, high protein feeding, and in diseases affecting the muscles. This chapter is most fascinatingly written, and Professor Hunter, who has himself contributed much work on these questions, is to be congratulated on it.

In a similar manner praise must be given to other chapters which deal with the discovery, the synthesis and constitution of creatine and creatinine, the chemistry of these two substances and their derivatives, their preparation and quantitative estimation, their biological distribution (mainly based on Folin's quantitative methods), their output coefficient and metabolic significance, their physiology and origin. The last-named chapter, dealing with the origin of creatine and creatinine, although of necessity highly speculative, makes interesting reading, if only in showing how little we really know of the origin and fate of the chemical

products which take part in the metabolism of the normal as well as the abnormal organism. However, Professor Hunter has succeeded in throwing light even on this field, and this with remarkable caution.

Reference must also be made to the bibliography of 30 pages and the excellent index, which seems to be free of error, which can very rarely be said of the indexes to scientific books.

M. NIERENSTEIN.

FERTILISERS AND FEEDING STUFFS ACT, 1926. By H. J. JOHNS. Pp. 185. London: Butterworth & Co. Price 10s. 6d. net.

This book reproduces the Fertilisers and Feeding Stuffs Act, 1926, and also contains an explanation of many of its provisions. As the author was the secretary of the various committees whose work finally resulted in the Act and its Regulations, there probably was no one more fitted for the task of writing an explanatory work on the provisions of the Act.

The responsibilities and duties of a seller, and the necessary steps to be taken by a purchaser to avail himself of the protection afforded by the Act, are clearly set out. Few can deny that the provisions of the Act are cumbersome. But in the sale of fertilisers and feeding stuffs there appear to be so many interests involved, that to render fraudulent sales punishable, without great inconvenience to the trade generally, presents an almost insurmountable difficulty. Therefore, marks, statutory statements, and labels containing particulars, etc., came into existence, and whilst the introduction of these terms may have been difficult to understand in the past, the necessity and the reason for them is made clear, and the duties of the manufacturer and merchant respecting them outlined in the work.

Probably to the analyst the most important pages dealing with the main provisions of the Act are those which contain a tabled summary of offences. It cannot be denied that, unless close touch is kept with the Act, difficulty will be experienced in ascertaining what omissions, etc., constitute an offence, and what action should follow an offence after detection. The summary referred to above gives very concisely the necessary procedure in all circumstances. The Schedules of the Act are printed in full and are self-explanatory. The Regulations made under the Act occupy nearly 40 pages, and they contain the practical portion of the work devolving upon an official agricultural analyst. The analytical processes contained in the Regulations of the Fertilisers and Feeding Stuffs Act, 1906, have been, to a large extent, reproduced in the more recent Regulations, but in a number of instances alternative processes have been included. The work terminates with an appendix containing the circular letters which have been distributed by the Ministry.

The book is of unquestioned importance to all officers concerned with the administration of the Fertilisers and Feeding Stuffs Act. It lucidly explains the provisions of the Act and embodies all the official information relative thereto, to date.

F. W. F. ARNAUD.

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

THE Annual General Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, March 6th, The President, Mr. Edward Hinks, was in the Chair.

The Hon. Treasurer presented the accounts of the Society for 1928, and votes of thanks were passed to the Hon. Treasurer and the Hon. Secretary.

Messrs. Marreco, Houseman & Brandon, Chartered Accountants, were appointed auditors of the Society's accounts for 1929.

The President delivered his Annual Address. Mr. E. R. Bolton moved that a hearty vote of thanks be accorded to the President for his address, and that his permission be asked to print the address in *THE ANALYST*. This was seconded by Dr. G. W. Monier-Williams, and the motion was carried.

The following were elected as Officers and Council for the year 1929:

President.—Edward Hinks.

Past Presidents, serving on the Council.—E. Richards Bolton, A. Chaston Chapman, Bernard Dyer, P. A. Ellis Richards, G. Rudd Thompson, E. W. Voelcker, J. Augustus Voelcker.

Vice-Presidents.—John Evans, J. T. Hewitt, T. Macara.

Hon. Treasurer.—E. B. Hughes.

Hon. Secretary.—F. W. F. Arnaud.

Members of Council.—A. P. Davson, E. V. Jones, R. Lessing, A. More, W. Partridge, C. A. Seyler, J. T. Dunn, N. Evers, G. Roche Lynch, C. J. H. Stock, J. R. Stubbs, Geo. Taylor.

An Ordinary Meeting of the Society then followed, the President, Mr. Edward Hinks, being in the chair.

Certificates were read for the first time in favour of:—Peter Trevisa Clarke, B.A., Alfred Clive James, B.Sc., A.I.C., Herman Lee, B.Sc., A.I.C., James Frederick Morse, Lawrence John Odling, Willie Horner Wilkinson.

Certificates were read for the second time in favour of Frank Atkins, Edmund Baron Bennion, M.Sc., A.I.C., John Haslam, M.Sc., A.I.C., Stanley Gordon Kenrick, B.Sc., A.I.C., Bryn Jones, B.Sc., A.I.C., John Upton Lewin, B.Sc., A.I.C., and Leslie John Walker.

The following were elected Members of the Society:—William Bennett Adam, M.A., A.I.C., Alfred Louis Bacharach, B.A., F.I.C., Andrew Dargie, B.Sc., A.I.C., and Wadie J. Itayim.

The following papers were read and discussed:—"The Alkaloid Test for Tannin," by Christina Mary Fear, B.Sc. (work done under the Analytical Investigation Scheme); "The Cryoscopic Method for the Detection of Added Water in Milk," by A. L. Andrew; and "Investigations on the Relations between the Acidity and Freezing Point of Milk," by Alfred J. Parker and L. S. Spackman.

NORTH OF ENGLAND SECTION OF THE SOCIETY OF PUBLIC ANALYSTS.

THE Fourth Annual General Meeting was held on March 1st in Manchester. In the absence of Dr. Dunn, Mr. J. Wood presided, and fourteen members were present. The following committee was elected for the coming year:—Mr. S. E. Melling (Chairman), Mr. G. D. Elsdon (Vice-Chairman), Messrs. R. F. Easton, H. T. Lea, H. M. Mason, J. Miller, Prof. Roberts, J. P. Shenton.

Mr. J. R. Stubbs was elected Hon. Secretary and Treasurer, in place of Mr. H. T. Lea, who resigned. Messrs. Marshall and Coates were re-elected Hon. Auditors.

A paper was then read on "The Examination of Further Samples of Milk by the Refractometer," by G. D. Elsdon, B.Sc., F.I.C., and J. R. Stubbs, M.Sc., F.I.C.

Annual Report of Council

March, 1929.

THE Roll of the Society stands at 600, the Society having a larger membership than at any previous time.

During the past year the Council has had to report, with regret, the deaths of the following members:—

Benedict Kitto (Obituary, *THE ANALYST*, 1928, 53, 314).
W. P. L. Hope (Obituary, *THE ANALYST*, 1928, 53, 567).
M. S. Salamon (Obituary, *THE ANALYST*, 1928, 53, 568).
A. Smetham (Obituary, *THE ANALYST*, 1928, 53, 566).
J. H. B. Jenkins (Obituary, *THE ANALYST*, 1929, 54, 73).
J. West Knights (Obituary, *THE ANALYST*, 1929, 54, 132).
Frankland Dent.*
T. P. Blunt (Obituary, *THE ANALYST*, 1929, 54, 133).
G. Watson Gray.*

The above names include that of Alfred Smetham, who was President of the Society during the years 1920 and 1921.

* Obituary notices will be published later.—EDITOR.

During the year, seven meetings of the Society were held, and the following papers were communicated:—

- "Composition of the Fatty Acids present as Glycerides in Elasmobranch Oils." By Professor T. P. Hilditch, D.Sc., F.I.C., and A. Houlbrooke, M.Sc.
- "Behaviour of Indicators in the Titration of Ammonia, Sodium and Calcium Phosphates, the Methylamines, Pyridine Bases and Boric Acid." By R. T. Thomson, F.I.C.
- "Cacao Tannin." By H. R. Jensen, M.Sc., F.I.C.
- "Coffee Parchment as an Adulterant of Bran and Sharps." By John Evans, F.I.C., and T. E. Wallis, B.Sc., F.I.C.
- "Determination of the Colour-producing Constituents of the Cacao Bean." By W. B. Adam, M.A., A.I.C.
- "Determination of Vanadium in Steel." By A. T. Etheridge, Ph.D., F.I.C.
- "Colorimetric Determination of Antimony and its Separation from Tin." By S. G. Clarke, B.Sc., A.I.C.
- "Determination of Carbon Dioxide in Soils." By A. Riad, B.Sc., Ph.D.
- "Locust Kernel Gum and Oil." By A. L. Williams, A.I.C.
- "Investigations into the Analytical Chemistry of Tantalum, Niobium and their Mineral Associates. XII, Observations on the Pyrosulphate Hydrolysis Method." By W. R. Schoeller, Ph.D., and E. F. Waterhouse.
- "The Separation of Lead Tetra-Ethyl from Solution in Petroleum Spirit." By F. W. Toms, F.I.C., and C. P. Money, B.Sc., A.I.C.
- "A New Precipitation Method for the Determination of Vanadium, and its Application to Steel Analysis." By B. S. Evans, Ph.D., F.I.C., and S. G. Clarke, B.Sc., A.I.C.
- "Method for the Analysis of Liquorice Mass." By P. Houseman, Ph.D., F.I.C.
- "Polarimetric Determination of Sucrose in Milk and Sucrose Mixtures." By G. W. Monier-Williams, O.B.E., Ph.D., F.I.C.
- "The Analysis of Starch Sugar Degradation Products by Selective Fermentation." By T. McLachlan, F.I.C.
- "Investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates. XIII, A New Method for the Separation of Zirconium and Hafnium from Tantalum and Niobium." By W. R. Schoeller, Ph.D., and E. F. Waterhouse.
- "Improved Method for the Determination of Small Quantities of Antimony in the Form of Stibine." By Julius Grant, M.Sc., A.I.C.
- "Determination of Unsaponifiable Matter in Oils and Fats." By E. Lester Smith, M.Sc., A.I.C.
- "Composition of Irish Butter." By Paul Arup, M.Sc., F.I.C.
- "Volumetric Determination of Mercury." By H. B. Dunncliff, M.A., Sc.D., F.I.C., and H. D. Suri, M.Sc.
- "The Occurrence and Determination of Boron Compounds in Vegetable Products." By A. Scott Dodd, B.Sc., F.I.C.
- "The Determination of Small Quantities of Alcohol in the Human Subject." By John Evans, F.I.C., and A. O. Jones, M.A., F.I.C.
- "The Analysis of Mixtures containing Acetone, Ethyl Alcohol and Iso-propyl Alcohol." By C. A. Adams, B.Sc., F.I.C., and J. R. Nicholls, B.Sc., F.I.C.
- "The Specific Gravities and Immersion Refractometer Readings of Dilute Mixtures of Acetone and Water." By J. R. Nicholls, B.Sc., F.I.C.
- "The Wijs Method as the Standard for Iodine Absorption." By J. J. A. Wijs.
- "The Fatty Acids and Component Glycerides of some New Zealand Butters." By T. P. Hilditch, D.Sc., F.I.C., and Eveline E. Jones, M.Sc.

"A New Test for Boric Acid and Borates." By A. Scott Dodd, B.Sc., F.I.C., F.R.S.E.

"The Determination of Beryllium in Rocks." By B. E. Dixon, M.Sc., A.I.C.

The sales of *THE ANALYST* have continued to increase, indicating the useful character of the matter published.

Reference to the Treasurer's Statement, published separately, shows that the continually increasing cost of our publication and other expenses have again been successfully met.

The Council has continued to act with the Institute of Chemistry with regard to the terms of appointments of Public Analysts. A statement relative to the conditions of appointment, etc., of Public Analysts and of Official Agricultural Analysts was prepared by a Sub-Committee of the Public Appointments Committee of the Institute of Chemistry. The statement was forwarded to the Royal Commission on Local Government as representing the views of the Institute of Chemistry and of the Society.

A Committee consisting of representatives of the Society and of the Association of British Chemical Manufacturers issued its report concerning the maximum permissible amounts of arsenic in colouring matters used in foodstuffs. (See *THE ANALYST*, 1928, 53, 217.)

The Society was approached by the Metropolitan Branch of the Society of Medical Officers of Health with regard to a suggested legal definition of ice-cream which had been submitted to them by a trade association. The Council did not agree with the definition and suggested the lines upon which legislation on this matter was desirable.

Consideration was given to the Food and Drugs (Adulteration) Bill which subsequently became law. Representations were made to the Joint Committee of both Houses of Parliament, with the result that certain clauses were amended.

The Society has now retained the services of Parliamentary Agents to advise them of the introduction of all Bills which might be likely to be of interest to the Society.

The four Sub-Committees constituted by the Standing Committee on Uniformity of Analytical Methods are at work on the problems submitted to them, namely:

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|---------------------|---|
| (1) Essential oils. | (3) Dirt in milk. |
| (2) Milk products. | (4) Metallic contamination of food colours. |

Although these Sub-Committees have issued no report during the year under review, it is expected that further reports will be forthcoming at an early date.

Work under the Analytical Investigation Scheme has been continued. The reports of three investigations have been received, six problems are still being investigated, and two grants from the Fund have been made.

The Council considered the Reconstituted and Synthetic Cream Bill, 1928, introduced into the House of Commons, and communicated with the promoters of the Bill expressing disagreement with some clauses. The Bill was withdrawn.

EDWARD HINKS, *President*.

F. W. F. ARNAUD, *Honorary Secretary*.

Annual Address of the President.

(MR. E. HINKS, M.B.E., B.Sc., F.I.C.)

Delivered at the Annual General Meeting held on March 6th, 1929.

LADIES AND GENTLEMEN,

The past year has been one of great legislative interest to this Society, and it seems to me fitting that I should devote to this subject the remarks which it is my privilege to address to you this evening.

The legislation to which I shall mainly refer deals with food for man or beast and with fertilisers for the soil. These matters are not of immediate concern to many of our members in their professional capacity, but they are of moment, directly or indirectly, to a larger number than those who are themselves engaged directly in the work of the Public Analyst or the Official Agricultural Analyst. I would ask the indulgence of those who are not so concerned. Their time will come. It may not be long before we have a Metals and Ores (Sophistication) Act; perhaps we may soon have the Rare Earths (Tantalum, &c., in Titanium) Regulations. In fact, our metal specialists may even now be called upon to determine whether, within the meaning of a Merchandise Marks (Imported Goods) Order, a safety razor blade, or a ball bearing, or a zinc sheet has been made in Great Britain or has been imported, or whether the indication of origin given is a correct one or not—a problem which is of the same order of difficulty as that of determining whether an egg was produced on a farm in Denmark or a farm in Devonshire. This is not entirely a fanciful picture: Orders dealing with these articles, and scores of others, are in force, though to what extent Analysts will be called upon in the execution of them is uncertain.

It is remarkable that within the space of one year the two main Acts of Parliament with which we are officially concerned have been repealed and new Acts have come into force, the Fertilisers and Feeding Stuffs Act of 1926, and the Food and Drugs (Adulteration) Act of 1928, whilst it was within the same period that the Public Health (Preservatives, &c., in Food) Regulations, in their present form, gradually introduced, came into the plenitude of their power.

With regard to the Adulteration Act, 1928, piety should compel us to remember that the Sale of Food and Drugs Act, which it replaces, was the direct cause of the foundation of this Society. The Society's activities now cover a much wider field, and its membership embraces chemists engaged in every branch of analytical chemistry, and even wider still, chemists who, though not practising as analytical chemists themselves, realise the fundamental importance of analytical chemistry. But, looking back, we see that the old Sale of Food and Drugs Act of 1875, just repealed, was the spark that brought this Society to life. Were this a dinner instead of an Annual General Meeting we should be drinking in silence the toast "In piam memoriam fundatoris nostri."

There is other legislation, to which I shall refer later, but for the moment may I confine myself to a consideration of these two Acts—the Fertilisers and Feeding Stuffs, and the Food and Drugs (Adulteration) Act.

It is of interest to note the different manner in which these two Acts have been treated. The Fertilisers and Feeding Stuffs Act was repealed and an entirely new Act, based to a large extent upon a new principle, was put in its place. It is not my intention to discuss this Act in detail—such a discussion would indeed occupy the whole of the time at my disposal. It is a complicated Act, and an inspector appointed under it has my sympathy. We wish it, I am sure, success. Time will show whether it will prove to be successful in having removed what were considered to be faults in the old Act and in ensuring to the farmer and his farm that protection which it is the object of the Act to ensure. I will refer only to matters of principle, and the main change of principle involved is the complete divorce of the civil and criminal procedure under the Act. Any sample taken at the farm can be the basis of civil claims only, whilst criminal proceedings can follow only upon the taking of a sample at the premises of the seller, before delivery to the ultimate purchaser takes place.

The Food and Drugs Acts, and some of the kindred Acts, were not altered in principle or amended in any way, but were submitted to a process of consolidation. Consequently, if they had faults and deficiencies, those faults and deficiencies remain. I have not been able to see myself, neither have I found anyone who has discovered, the merits of this consolidation. Moreover, consolidation is a difficult process, and there is in my mind the horrid fear that in this difficult process some wording has been altered, or a word omitted or inserted, which will give the ingenious legal mind, which, we may be sure, is being directed to the matter, an opportunity of making the new Act inoperative. The future will show whether or not this fear is ungrounded—I trust it is. Certain it is that the alteration in form of a few words has reintroduced an old difficulty which, in its day, required an amending Act for its removal. History may have to be repeated: I will not prophesy, especially with regard to a legal point.

Why have these Acts had such different histories?

It is plain that, though in essence the relations between the seller and purchaser of a fertiliser and feeding stuff or of food are the same in either case, the method of treatment of these relations must be different in the two cases. The vast number and the small bulk of most purchases of foods, as compared with those of feeding stuffs and fertilisers, alone is responsible for differing treatments of the relation. I do not know that this alone is responsible for such widely differing treatments as are to be observed. Incidentally, a curious difference in viewpoint is that, under the Food and Drugs Act, the requirement is that the article should be of the nature, substance and quality demanded, whereas, in the case of the Fertilisers and Feeding Stuffs Act, the requirement may be that the guarantee shall be in accordance with the article sold, a difference which, to my mind, makes it very difficult to frame a certificate strictly in accordance with the latter requirement.

This, however, is rather a matter of detail. Of greater significance is the fact that, under the Fertilisers and Feeding Stuffs Act, there is established an Advisory Committee, carrying on the work of the previous Committee which advised on technical matters before the Act was drafted. This Committee advises the Minister on the question of Regulations made under the Act. Further, there are established under the new Act, as under the old, definitions, statutory guarantees of important constituents, and methods of analysis. Moreover, and it is most important to note this, the Advisory Committee continues in being, and provision is made for alteration of the schedules, definitions and methods of analysis as occasion may require. It is, I think, true that the definitions are meagre and, if I may criticise them, not very illuminating, but for the moment I concentrate upon the principle. Why should not these principles be adopted, and widely adopted, in Food and Drugs legislation? Admitted that in the case of foods the variety of article is greater, and admitted also that in a piece-meal manner some definitions and standards have been established, one or two by the Minister of Agriculture under the Food and Drugs Act, a few more by the Minister of Health under the Public Health Acts. Whilst acknowledging the help that these have been, I feel that only the fringe, or not much more than the fringe, has been dealt with. An Advisory Committee or Committee of Reference for Food Legislation has been advocated by Departmental Committees, by a Royal Commission, and by this Society.

Is it faulty reasoning to argue that, if such principles can be incorporated in one Act, so can they be, if desirable, in the other? Perhaps the dimension of the problem with regard to food for human consumption is a reason for the difference in treatment of the two questions: it can hardly be considered a sufficient reason for leaving the matter alone.

Presumably the Fertilisers and Feeding Stuffs Act, as an Act, will stand as it is for some time. Can the same be said of the Food and Drugs (Adulteration) Act? And, if it can, is it desirable that the legislation should stand as it is?

And here I would refer to an address, given in June of last year by Mr. Haygarth Brown, of the Ministry of Agriculture, to the Incorporated Society of Inspectors of Weights and Measures, entitled "On Quasi-criminal Offences." This is of much importance, as it was an expression of the views of a high official in the Ministry of Agriculture: perhaps, I do not know, similar views are held in other Ministries, and Ministries are very powerful in the shaping of legislation. Mr. Haygarth Brown's main thesis is, that there is a growing revolt against the "quasi-criminal offence"; by which I understand him to mean a revolt against the principle of offences under Public Control laws, such as the Food and Drugs Acts, being criminal offences. I think we shall all agree that there are occasionally offences against the Food and Drugs Act which should hardly be stigmatised as criminal offences—I wish it to be understood that I use the word "criminal" in a popular sense and not the legal sense—but, on the other hand, I think we shall all agree that offences which involve fraud are criminal offences. There is, I admit, a distinct difference between selling an article which has fallen naturally, and perhaps

quite unsuspectedly, below some legal limit, and the action of deliberately adulterating. But who is to decide which of these two things has happened except the Courts, even if they can?

Mr. Haygarth Brown founds many arguments on what he calls the "tinned food offence," when a retailer gets into trouble for an offence which really is committed by a manufacturer; he does not mention warranty defence, but it will be allowed, I think, by everyone that, granted an offence, the real offender is the person upon whom should fall the opprobrium of meeting the charge.

Mr. Haygarth Brown seems to blame the Acts of Parliament for creating offences and thereby creating offenders. In a way, of course, it may be argued that the law creates an offence, but, if we look deeper, is not the offence already there? Take the case of the Preservatives Regulations. The assumption underlying these Regulations is that chemical preservation of food may be, and if practised to an excessive extent, is, injurious to the health of the consumer. Or take the case of Butter Regulations. Selling butter containing an excessive proportion of water is prejudicial to the purchaser's pocket and, to the extent to which the excessive addition is made, is prejudicial to his health. Can we allow that it is the Regulations that create offences and thus create offenders, who, if it were not for the Regulations, would be doing nothing wrong? Was short weight always wrong, or did it only become wrong—and did having unjust scales and measures only become wrong—when Acts of Parliament made such things offences?

It is clear, on the other hand, that some legislation does create offences in matters in which there was no suggestion of offence or wrong before. The Merchandise Marks Act, 1926, does this. No one can suggest that before the Regulations were made under this Act there was anything morally or legally wrong in selling an imported article without declaring it to be such, and marking it as such. With certain specified articles this Act has now created this offence.

However, in a complicated civilisation, public control legislation would appear to be necessary, and, within reason, beneficial. It may be carried to excess, but it would be the greatest mistake to undermine such important and essential legislation as the Food and Drugs, and kindred Acts, because there may be excesses in legislative control of the citizens' and the traders' activities—and a revolt against such excesses.

Mr. Haygarth Brown discusses methods of procedure, alternative to the present "quasi-criminal" procedure, but it is difficult to see in them any hopeful programme which would placate those, if there be any, who object to the procedure of the Food and Drugs Act, and, at the same time, afford adequate protection to the purchaser, worthy, however, of study as is the paper to which I have referred. It must not be forgotten, and I think it is sometimes forgotten, that it is the purchaser's interests which are primarily to be protected.

In parenthesis, I would mention the question of drugs. We are all looking forward to a new edition of the British Pharmacopoeia. If this is delayed, I, for one, would not complain. We can all appreciate, from a distance, the amount of

work that is necessary for revision and amendment. But what of its position in relation to the Food and Drugs Act?

In many of the Dominions the British Pharmacopoeia is the statutory standard for drugs under the Food and Drugs legislation: in this country, the country of its origin, it is not: perhaps this is another case of a prophet not being without honour save in his own country. The Committee of Civil Research (Sub-Committee on the British Pharmacopoeia) has considered this matter. The fact that the Pharmacopoeia has been accorded a definite statutory position overseas, the Committee considered to be "a tribute to the authority of the work which we recognise with satisfaction." The Committee, however, reports definitely against giving it a similar position here. To quote from this Report: "The topic is one which is scarcely within our terms of reference, but as we have considered it we may be permitted to express our opinion, which is that no legislative action is called for in this country. . . . Indeed we are apprehensive that an attempt to give a specific legal sanction to the Pharmacopoeia might do more harm than good. We see practical difficulties in making the Pharmacopoeia an absolute legal standard for the articles mentioned in it, and indeed the work is not designed to serve this object." I suggest that the point is rather, could it not, and should it not, be so designed? However, what I have quoted is the authoritative opinion of the Committee of Civil Research, so, presumably, the somewhat equivocal position of the Pharmacopoeia in relation to Food and Drugs legislation will remain.

I have referred to these legal, and ethical, matters for the purpose of my argument, which is, that with regard to future legislation, in particular Food and Drugs legislation, this Society should have, and should have ready, a policy.

In the year 1894 the Council of this Society produced a complete draft of a Sale of Food and Drugs Act. I was much surprised to find it, as I did, one day when I was glancing through old volumes of the ANALYST. Some of our senior members here this evening must have taken part in framing that draft Act.

Personally, I do not think that the Council should attempt to repeat that effort. If we have any new principles which we think should be adopted, if there are changes in procedure which our experience shows to be advisable, let us urge these and leave to others their incorporation in a Bill. But let us beware of decrying the existing Act, or Acts, and then being found wanting when we are appealed to for concrete suggestions for amendment. I am fairly familiar with the proceedings of this Society for a number of years now, but, if I were appealed to at this moment to say what is the policy of the Society, I should find it difficult to give an answer.

There are the big questions of definitions and standards. What is the Society's policy in regard to these? As I have mentioned, there are many definitions under the Fertilisers and Feeding Stuffs Act. How many are there, under the Food and Drugs Act? A cotton cake for cattle must contain, within one-tenth, the amount of oil which it is declared to contain, and its oil content must be declared: a cream for human consumption must contain, how much oil or fat? I do not know: no one knows. All we know is that it does contain anything, say, from eighteen to eighty

per cent., or nearly those figures. Standards and definitions—if we had more definitions we should hear less of the innocent manufacturer being pilloried in the Police Court, an infliction with the contemplation of which you were harrowed from this chair two years ago. I have every sympathy with the manufacturer who is trying to produce at a competitive price a sound, wholesome article: but, at the same time, I have equal sympathy with the Public Analyst who, seeing what he thinks at any rate to be wrong, after making such enquiries, investigations and efforts in other directions as he can, has to put the matter to the test, or let things slide. The fault lies, I submit, with the vagueness of the legislation under which the Public Analyst has to work.

For our consideration there are the questions of the pre-packed or tinned article—the responsibility of the retailer and the manufacturer—and of labelling, which is of great importance, though one wonders to what extent the public reads labels. Does the Society still consider that a body such as a court of reference or advisory committee should be formed, and what form should it take? There is the much-debated question of prescribed methods of analysis. Then, again, there is the control of the purity of substances entering into the composition of food. Cases must arise in which such control can hardly be exercised by analysis merely of the finished article. The purity of food colours is such a case. A similar problem arises under the Preservatives Regulations—it is not possible, by analysis of the finished article, to determine whether a preservative has been added to a non-scheduled compounded article, which would be a breach of the Regulations, or whether it has been introduced through the use of an ingredient which is itself a scheduled article in which the preservative is permitted. Hence arises the necessity for right of entry, conceded in certain circumstances by the Preservatives Regulations and by the provisions in the Act relating to butter factories.

There is the very difficult question of the control of the vitamin activity of foods, or the checking of statements made about that activity. How is such control to be exercised? Some may think that, in this rapidly developing and changing realm of enquiry, it is too early at present to attempt to establish legal control. I am afraid that it is the difficulty of the question, rather than any lack of need for its consideration, that is a determining factor. There has, as you know, been one case under the Food and Drugs Act where vitamin activity was the issue; it would appear to be certain that before long it will become a very big issue.

It is on these matters that the Society should attempt to have a policy. I say "attempt," because it is possible that on some of them agreement could not be reached. It might be that Public Analysts on the one hand, and other analytical chemists on the other, might think differently. Towards the end of last year there occurred such an event, in which the Society, as such, was not at first officially concerned, but in which a number of its members were. Agreement has not yet been reached.

I do not mean that there is antagonism between those whom I may term the official chemists and the manufacturers' chemists. Two years ago Mr. Bolton referred to the way in which this Society had brought the two bodies of chemists

together to live and work in harmony. I fully endorse what he said on that point. Nevertheless it is possible that there may be some divergence of views. This Society, for the very reason that its members are working in very different fields, should, at any rate, be able to view all sides of these questions. Seeing all sides of a question has, however, its drawbacks as well as its advantages.

This matter of having a policy is one which I commend to the new Council elected this evening, for their immediate and earnest attention.

There are now some other Acts of which mention must be made. The Sale of Food (Weights and Measures) Act, 1926, which is, I believe, now fully in force, concerns sale by net weight. There are three schedules, enumerating some 30 articles of food to which the Act applies. Analysts will, no doubt, be consulted as to whether the article sold is or is not suet, is or is not bean flour, and so forth.

The Merchandise Marks Act, 1926, I referred to incidentally earlier; it relates to the marking of the country of origin of imported goods. Eight articles of food are at present affected and scores of other articles. I do not know how these Orders are going to be enforced—possibly it will all be done at the port of entry, but it is significant that, with regard to articles of food, Food and Drugs Authorities are empowered to take samples—what is to be done with the samples is obscure. The problem raised here is the differentiation of home, foreign and Empire apples, honey, eggs, dried eggs, oat products, etc., mowing machines, gloves, glue, artificial teeth (artificial eyes are especially excluded), pumps, briar tobacco pipes, ladies' handbags, carbon paper, and so on, a regular stores catalogue.

The Agriculture Produce (Grading and Marking) Act raises similar problems, except that, in some respects, they are explicitly chemical—the differentiation of fresh, preserved, cold-stored and chemical-stored eggs. A respite is granted by an Order of the Minister of Agriculture exempting from the operation of Section 3 of the Act eggs preserved by cold storage or chemical storage because, the Minister says, "it is not possible to ascertain by analysis whether eggs have, in fact, been kept in cold storage or chemical storage." Eggs preserved by immersion in lime water, water-glass or oil do not get exemption.

The Safeguarding of Industries Act, though now many years old, has, no doubt, produced its annual crop of problems for the Government Chemist.

One further small point. By Statutory Rules and Orders No. 975, 1928, under the Silicosis scheme, Workmen's Compensation Act, silica rock by definition does not include any rock containing less than 50 per cent. of free silica, whilst for other purposes under the scheme the limit is 80 per cent. of total silica.

It is more than probable that I have mentioned only a proportion of these modern legislative enactments and regulations—and the flood of orders may continue.

Now what is the lesson to be learnt from all this? It is, surely, that the services of the analytical chemist are to be called upon to an ever-increasing extent. I have referred to the ethical side of some of the legislation—that is not particularly the business of the Society; then I spoke of the necessity of having a policy,

especially with regard to Food and Drugs legislation—that is more our business; but our main function is the advancement of analytical chemistry, and it is in this direction that our main efforts should be directed. The efficacy of much of the legislation I have spoken of depends upon our ability as analysts.

As you know, certain problems are in the hands of Sub-Committees convened by the Society. An enormous amount of work has been done by the Sub-Committees, but the rate of progress is disappointingly slow. I am not, I think, betraying any confidences when I say that one cause of the slow progress is the surprising extent of the experimental differences or errors disclosed when a number of analysts employ the same analytical process, often a process that has been intensively studied. As these Sub-Committees are working under a scheme for the uniformity of methods of analysis, uniformity of results is one of the essentials.

But whatever problems are being investigated by these or other Committees, by official or semi-official bodies which are or may be formed for specific purposes, individual members of this Society are not relieved of the responsibility of individually contributing to the solution of the many problems that confront us. Mr. Chaston Chapman, in his admirable address to you in 1915, quotes an eminent chemist, whom he kindly omits to name, as saying "Analytical chemistry presents no further problems"—I quote Mr. Chapman's refutation, "A statement more wide of the mark could scarcely be imagined." The popular view of analysis, and apparently the view of that "eminent chemist," would seem to be that by analysis a material is infallibly separated out into neat little heaps of the various constituents, which heaps can then be conveniently weighed or measured; this view must, I think, account for the existing marked disinclination to disclose to the analyst anything about the material to be analysed. How different the reality—how often is an analysis, with all the knowledge that we have, and it is not inconsiderable, yet an adventure through unexplored or, at any rate, very imperfectly mapped, territory. Even the well-trodden paths have a disconcerting tendency to become slippery and to afford an insecure foothold, or they become entangled with undergrowth and obscure; often, by degrees or abruptly, the path is no more a path, it is lost in the jungle. Is it an exaggeration to say that even butter is on a slippery part of the path and, with many other things, jam is in the jungle? Of course, thanks to the labours of those who have gone before and those who are here now, we can do some things, and do them very well. But the labours must be continued, and every branch of chemical science must be impressed into the service of analytical chemistry.

We can fulfil what I have described as our main function in relation to legislation only by research; the abrogating order of the Ministry of Agriculture referred to just previously comes aptly to point the moral. There is need for imaginative research of a very high order; there is room also for research of a humbler nature. The President of one of the Sections of the British Association last year, in speaking of research, coined what is, I think, a very arresting phrase, "If there is one thing worse," he said, "than a mediocrity who does no research, it is a mediocrity who does." By that I do not think that he meant to decry honest,

useful research of a humble character; it was, I should think, rather a protest against the person who labels himself as a research worker because he has neither the ability, nor the skill, nor the character to do anything else.

When one looks at the number of communications to this Society, one cannot be satisfied that nearly all that should, and could, be done is being done. The Society, and Analytical Chemistry, is indebted to private members, to the Government Chemist and his department, to the Chemist at the Ministry of Health, to chemists in other Government departments, and to a number of chemists at Research Association laboratories, for many very valuable contributions.

I should like to take this opportunity, too, of expressing appreciation of certain enlightened commercial firms who are liberally giving the services of their chemists and the resources of their laboratories for the purpose of investigations, in which we, and they, are interested.

There is hardly a single substance with which we have to deal which does not require investigation; there is hardly a process which by investigation cannot be improved; many substances and many processes cry aloud for this investigation. It is pleasant to be able to record that, under our Analytical Chemistry Research Scheme, three reports have been received during the year, and that six problems are in hand. I suggest, however, that amongst our members there are many who could contribute to the resolving of some of our uncertainties but do not do so.

I have directed your attention this evening to legislation and our relation to it. Quite apart from other fields in which chemical analysis is of fundamental importance, it is clear that in the fields covered by legislation more and more will be demanded of the analytical chemist. It is for us to see that, up to the limits of possibility, that demand is met; and for the future it can be met only by investigation and research.

The Cryoscopic Method for the Detection of Added Water in Milk.

By R. L. ANDREW.

(Read at the Meeting, March 6, 1929.)

DURING the last twenty years numerous papers on this subject have been published. So far as the writer is aware, none of these deals with the use of the method, over a period of years, as a routine test in the examination of milk samples. It was therefore thought that a description of the test, as employed in the Dominion Laboratory, New Zealand, would be of value.

Interest in the method was aroused by a paper entitled "The Freezing Point of Milk, its use in the Detection of Added Water," by J. B. Henderson, Government Analyst, Brisbane, Queensland, which was published in the Proceedings of the Australasian Association for the Advancement of Science, 1909, p. 159. In this paper Henderson stated that after experimenting with milks of known purity, and with milks with known amounts of added water, he adopted the method for samples obtained by inspectors under the Health Act.

A careful investigation seemed warranted, and a number of genuine milks from various farms were examined in this laboratory. The samples were taken throughout the year, the greater number being obtained during winter and spring. Both morning and evening milks were sampled. Good and poor farms were visited. In some cases samples were obtained from individual cows; in others the sample was from the mixed milk of two to twelve cows. The inspector in every instance watched the milking of the cows, and satisfied himself that no adulteration was possible. In all, 270 samples were obtained. The usual analysis of each for fat and non-fatty solids was made. The zero point of the thermometer was checked both before and after each set of observations. The acidity of the milk was also determined, to ensure that no appreciable souring (which would result in a lowering of the freezing point) had taken place.

As was to be expected, analysis disclosed wide variations in the fat and solids-not-fat. The fat ranged from 2.35 per cent. to 5.9 per cent. (though only ten samples were below 3.25 per cent., the legal standard for New Zealand). The solids-not-fat were from 8.06 to 9.43; eighteen samples were below the legal minimum (8.5 per cent.). The maximum variation of the freezing point was from -0.545°C . to -0.565°C . One sample only was above -0.550°C ., and five only below -0.560°C . With the other 264 the freezing point ranged from -0.550° to -0.560°C .

It would serve no useful purpose to publish the whole of the results, but a few which show gradations in fat and in non-fatty solids have been selected, and arranged in the following tables.

In Table I it is seen that large variations in the fat make no difference in the freezing point. This, of course, might be expected from theoretical considerations.

Table II shows a series of milks, varying somewhat uniformly in solids-not-fat from 8.06 to 9.43. The freezing points are all practically identical.

TABLE I.

Fat.	Solids-not-fat.	Freezing point.
5.90	8.59 per cent.	—0.550° C.
5.70	8.99 " "	—0.560° C.
5.17	8.95 " "	—0.560° C.
4.40	8.93 " "	—0.560° C.
3.70	9.15 " "	—0.550° C.
3.20	8.83 " "	—0.550° C.
2.90	8.32	—0.557° C.
2.65	8.95	—0.550° C.
2.35	9.15	—0.550° C.

TABLE II.

Fat.	Solids-not-fat.	Freezing point.
3.65	9.43 per cent.	—0.550° C.
3.95	9.29	—0.555° C.
4.20	9.12	—0.555° C.
3.80	8.88	—0.550° C.
3.80	8.67	—0.550° C.
3.15	8.50	—0.560° C.
3.20	8.33	—0.555° C.
5.20	8.26	—0.550° C.
4.00	8.16	—0.550° C.
4.70	8.09	—0.550° C.
3.45	8.06	—0.550° C.

These results were so favourable, that the method was adopted and has now been in use for fifteen years as a routine test, in the examination of milk samples submitted by inspectors under the Sale of Food and Drugs Act.

A description of the apparatus employed, the procedure in carrying out the test, and an account of its general use are given below.

APPARATUS.—The cryoscope employed is the simple form of Beckmann's Freezing Point Apparatus. The thermometer is of the usual Beckmann type, and is used for the one purpose only, thus avoiding the necessity of making frequent adjustments. The stirrer is made of fairly heavy brass wire, which is more suitable than the platinum stirrer usually supplied with the apparatus.

METHOD OF CARRYING OUT THE TEST.—Although the determination of a freezing point is a simple operation, it was found that much practice and strict attention to details were required if dependable results were quickly to be obtained. At first an attempt was made to carry out the test as recommended by Barthel in *Milk and Dairy Products*, p. 106 (1910), but difficulties were met with, and the procedure finally adopted was as follows:—The apparatus is filled with crushed

ice mixed with a small quantity of common salt, and in a separate vessel is placed a strong freezing mixture of ice and salt. The zero point of the thermometer is first ascertained by observing the freezing point of water. Sufficient distilled water to cover the bulb of the thermometer completely is placed in the freezing tube and the thermometer inserted. The tube is then placed directly into the strong freezing mixture, so that the surface of the water is just above the surface of the freezing mixture. The water is stirred slowly until a skin of ice is formed on the inside of the tube. The tube is then removed from the mixture, wiped with a dry cloth and warmed in the hand until the ice can be detached and broken up by means of the stirrer. The tube is then placed in the large tube of the apparatus and stirring continued. The mercury column falls slowly and finally remains stationary. The reading is now taken. In determining the freezing point of water some experience is necessary in order to arrive at the correct proportion of ice required in the freezing tube, and the degree to which it must be broken up.

To obtain the freezing point of milk the same quantity of milk is cooled in the strong freezing mixture. Super-cooling usually takes place, and immediately the mercury column begins to rise, the tube is quickly removed, wiped dry and placed in the large tube of the apparatus. Stirring is then continued until the mercury reaches its highest point and remains stationary. The reading is now taken, and is the freezing point of milk. With milk about one degree of super-cooling most usually takes place, and in these cases no correction is made. Occasionally there is greater super-cooling, and it has been found that the reading is then 0.01° C. too low for every extra degree of super-cooling. Sometimes it is difficult to obtain super-cooling. In such cases the mercury column becomes almost stationary at a point somewhat above the freezing point of the milk. At this stage the tube is removed from the freezing mixture, wiped, placed in the apparatus, and stirring continued. The mercury falls slowly, and finally remains constant. The reading is then taken, and agrees closely with that obtained after one degree of super-cooling.

I am aware that certain corrections should be made to obtain the true freezing point, but these have been intentionally omitted for the sake of simplicity and ease of working, and, as similar conditions are observed in each determination, the results obtained are strictly comparable. The procedure outlined above has the great advantage of simplicity both in apparatus and materials employed, while the manipulation required is reduced to a minimum. In practised hands twelve determinations per hour can be made, which compares very favourably in speed with other routine determinations, such as for fat and solids-not-fat.

At first readings to 0.001° C. were attempted, but experience showed that readings to 0.005° C. were sufficiently exact for practical purposes.

Samples giving any evidence of souring are rejected.

As far as possible all abnormal or apparently abnormal samples have been followed up and investigated. This has resulted in the accumulation of a series of most interesting results. As they afford particularly strong evidence as to the reliability of the test, a number of these investigations is given in detail.

1. A sample received from Napier contained:—Fat, 3·40; solids-not-fat, 8·50; and ash, 0·68 per cent. Freezing point, $-0\cdot500^{\circ}$ C.

At one time this milk would have been passed as complying with the standard, but the freezing point showed that it contained nine per cent. of added water. The inspector was advised as follows:—"The analysis of the sample showed that sufficient water had been added to bring the solids-not-fat just down to the standard (8·5 per cent.). It is very important that systematic adulteration of this kind be stopped, and samples from the farm would make our case quite conclusive." A sample of the mixed milk (evenings) was accordingly obtained at the farm and contained:—Fat, 5·20; solids-not-fat, 8·92; and ash, 0·75 per cent. Freezing point, $0\cdot550^{\circ}$ C.

If allowance is made for the additional fat in the farm sample, the solids-not-fat would be 9·1 per cent., which agrees closely with the percentage found in the original sample, when corrected for the added water.

2. A milk forwarded by the Health Department's inspector at Wanganui gave:—Fat, 4·50; solids-not-fat, 8·46 per cent.

As with the previous example, this milk would formerly have been passed as complying with the standard. The freezing point was, however, found to be $-0\cdot510^{\circ}$ C., showing that the sample contained 7·2 per cent. of added water. Prosecution was advised, and it is interesting to note, that it was then found, that the milkman had admitted adding water to the milk.

3. A sample received from Taranaki was found to be of the following composition:—Fat, 5·00; solids-not-fat, 8·85 per cent.; freezing point, $-0\cdot505^{\circ}$ C.

This was a milk of good quality, the proportion of fat being above the average, but the freezing point indicated that it contained 8·2 per cent. of added water. It was decided to investigate, and an inspector obtained at the farm samples representing both morning and evening milkings. Analyses resulted as follows:

		Fat. Per Cent.	Solids-not-fat. Per Cent.	Freezing point. °C.
Evening milk	..	4·50	8·63	$-0\cdot520$
Morning milk	..	4·85	8·81	$-0\cdot510$

These results appeared to show that the milk from this herd had an abnormal freezing point. The inspector was instructed to obtain further samples, and as it was found that on his first visit, he had not been able to watch all the cans, he was told to take an assistant with him. All the cans, as well as the milking were closely watched, and the analyses of the samples then obtained were:

		Fat. Per Cent.	Solids-not-fat. Per Cent.	Freezing point. °C.
Evening milk	..	5·80	9·16	$-0\cdot555$
Morning milk	..	4·85	9·55	$-0\cdot560$

The freezing point of the pure milk was thus proved to be normal. The composition of the original sample (when corrected for the 8·2 per cent. of added

water indicated by the freezing point) would be:—Fat, 5.45; and solids-not-fat, 9.64 per cent.

This agrees closely in solids-not-fat with the second sample of morning milk. Although the cows on the farm were all Jersey, it was thought that the milk was exceptionally rich. Subsequent experience has, however, shown that such milk is by no means unusual in districts where Jerseys predominate.

4. The analysis of a milk received from Palmerston North was:—Fat, 3.10; solids-not-fat (per cent.), 7.46 per cent.; freezing point, -0.510° C.; added water (calculated from the freezing point), 7.2 per cent.

Allowing for the added water, the unadulterated milk would be of the following composition:—Fat, 3.34; solids-not-fat, 8.04 per cent.

If this deduction were correct, the sample came from a herd yielding milk containing a percentage of solids other than fat below the legal standard (8.5 per cent. of solids-not-fat). Samples were obtained from the farm and examined, with the following results:—Fat, 3.70 and 3.15; solids-not-fat, 7.82 and 8.09; freezing point, -0.550 and -0.555° C.

These figures show that the deduction drawn from the freezing point of the original sample was correct. The milk came from a herd of Friesian cows, a breed which is known often to give milk of poor quality. The farmer was notified that he must not sell the milk for town supply, and he accordingly diverted it to a butter-factory.

5. Two samples obtained in Wellington were analysed, with the following results:—

	Per Cent.	Per Cent.
Fat	3.90	3.60
Solids-not-fat	8.26	7.98½

The freezing points were normal, indicating that the milks did not contain added water. Samples were obtained at the farm. The herd was a small one, and a sample of each cow's milk was obtained, as well of the mixed milk. Analyses resulted as follows:

	Cow No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	Mixed milk.
Fat, per cent.	4.00	3.90	3.65	3.40	4.20	3.80
Solids-not-fat, per cent.	8.12	8.22	7.12	7.98	7.88	7.90

The freezing points were all normal. These results confirmed the previous analyses, and showed that the freezing points correctly indicated that the milk was naturally poor and not rendered so by the addition of water.

6. A milk traced to a farm in the Hutt Valley gave the following results:—Fat, 4.20; solids-not-fat, 8.20 per cent.; freezing point, -0.550° C.

Although the percentage of solids-not-fat was below the standard, the freezing-point showed that the milk contained no added water. An inspector visited the farm and obtained single samples from the twenty-two cows comprising the herd. The herd was a mixed one, and the cows were in poor condition.

Most of the samples were below the average in quality, while four of them were very poor. The analyses of these were:

	Cow No. 6.	Cow No. 8.	Cow No. 10.	Cow No. 13.
Fat, per cent.	4.00	2.40	4.00	3.70
Solids-not-fat, per cent.	7.80	5.76	7.54	8.00
Freezing point	-0.555° C.	-0.550° C.	-0.560° C.	-0.560° C.

No. 8 is an abnormally poor milk. Examination by a veterinary surgeon showed that the four cows were all suffering from mammitis.

7. Three samples were obtained from a farmer at Otaki and analysed, with the following results:

	(1)	(2)	(3)
Fat, per cent.	3.70	4.40	4.30
Solids-not-fat, per cent.	7.08	8.22	8.62
Freezing point	-0.410° C.	-0.450° C.	-0.480° C.
Added water (calculated from the freezing point), per cent.	25.4	18.1	12.7

Allowing for the added water, the original milks would have the following composition:

	(1)	(2)	(3)
Fat, per cent.	4.96	5.37	4.92
Solids-not-fat, per cent.	9.49	10.03	9.87

These figures would indicate that the samples came from a herd giving exceptionally rich milk. Samples of the milk from each of the twenty cows in the herd were obtained at the farm, and the analyses fully bore out this supposition. The milk from individual cows contained abnormally high percentages of fat and of solids-not-fat, and the mixed milk of the herd was exceptionally rich. The results were:

Single cows.	Fat.	Solids-not-fat.	Freezing-point.
1	7.20	10.50	-0.560
2	7.40	10.70	-0.560
3	7.35	10.75	-0.565
4	7.00	10.02	-0.555
5	6.75	9.95	-0.565
6	5.60	9.90	-0.560
7	5.85	10.29	-0.555
8	5.70	10.28	-0.555
9	7.60	10.50	-0.560
10	8.40	11.40	-0.555
11	6.60	10.64	-0.560
12	7.05	10.13	-0.555
Mixed milk of 20 cows	5.40	9.70	-0.555

No. 10 contains a higher percentage (11.4) of solids-not-fat, than I have seen recorded for cows' milk. This herd was partly Jersey and Jersey cross, and several of the cows were being dried off.

The real value of the test is strikingly shown in the improvement brought about in the milk supply of Wellington City. Prior to the adoption of the test the sale of watered milk was a very common practice, and the milkmen knew that about seven per cent. of water could be added to average milk, without the risk of prosecution.

After its adoption the milkmen concerned very soon realised that the hands of the analyst had been greatly strengthened. Numerous cases were taken, and instead of offenders being charged with a deficiency, calculated on a standard of 8.5 per cent., solids-not-fat, the amount of added water was stated, usually seven per cent. more than that which would have been calculated from the standard. Many of the cases were keenly fought, but in no instance was the reliability of the test disproved or weakened.

The effect of such action was quickly reflected in the average solids-not-fat content of the milk sold in the city. The average solids-not-fat in 880 samples taken during 1910-1913 was 8.50 per cent. For the year 1916 (two years after the adoption of the test) the average had risen to 9.01 per cent. This average has since been maintained, being 9.02 per cent. over that of the ten years 1917-1926.

The account of the method of using the test has been given at some length, but that is necessary to illustrate fully all its advantages, which may be summed up as follows:

It provides a simple and reliable means of detecting added water in milk. It makes possible the prevention of the practice of adding sufficient water to rich milk to bring the solids-not-fat down to the legal standard.

It provides a means of distinguishing between naturally poor milk and milk to which water has been added.

From an experience extending over seventeen years, and as a result of thousands of determinations, and also from the investigation of apparently abnormal cases, I have concluded that the freezing point of genuine milk, determined in the manner described above, may be taken as not higher than -0.550°C .

If the freezing point of a sample rises to -0.530°C . watering may be suspected, and if to -0.520°C ., the milk has certainly been adulterated with approximately five per cent. of added water.

I should like to acknowledge the helpful advice given by Dr. J. S. Maclaurin (Dominion Analyst) in the early stages of the work, and the continued interest shown by him over the whole period.

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Investigations on the Relations Between the Acidity and Freezing Point of Milk.

BY ALFRED J. PARKER AND L. S. SPACKMAN.

(Read at the Meeting, March 6, 1929.)

IN the determination of added water in milk by the cryoscopic method, it is necessary to use a correction for the disturbing effect of acidity when testing "sour" milk (Monier-Williams, *Food Report*, No. 22, p. 3). The correction in use in this laboratory for some time had been that given by the "Connecticut Agricultural Experimental Station, 27th Report on Food Products (1922) (*cf.* ANALYST, 1924, 49, 280), namely, 0.003° C. for each 0.01 per cent. of acidity as lactic acid in excess of 0.20 per cent. Experiments made in this laboratory caused us to doubt the validity of the above correction, and the present investigation was therefore undertaken.

A sample of freshly drawn milk is taken, and its freezing point and acidity determined. The sample is then allowed to stand and become progressively more acid. The freezing point and acidity are now determined conjointly at intervals, and the results plotted on rectangular co-ordinate paper, with freezing point as ordinates and acidity as abscissae; then, if the above-mentioned correction be valid, the points will all lie on a straight line, the equation for this being:

$$T = [C(A - A')] + t \quad \dots \dots \dots (1)$$

where T is the observed temperature in degrees centigrade below zero; t , the normal freezing point of milk; C , a constant (in this case 0.003); A , the acidity (expressed as degrees of acidity); and A' , acidity of fresh milk (also expressed as degrees of acidity).

To simplify matters we used the Dairy Chemists' "Degrees" of acidity, according to which one "degree" corresponds to 0.01 per cent. of acidity as lactic acid.

The term "fresh milk" used hereafter, refers to milk, cooled at the farm and delivered to the city depot; our samples were taken on arrival, which, in the case of morning's milk, represented an interval between milking and sampling of about six hours, and the first tests were made as soon as possible after sampling. In the case of evening's milking an interval of about 4 hours elapsed between milking and sampling, and, after sampling, the samples were kept in a cool chamber (50° F.) overnight, and the first tests were made next morning.

At no time during our experiments did we have a *fresh* milk with an acidity as high as 20 degrees, practically every sample falling within the limits of 14 and 17 degrees; 31 per cent. of those examined had an acidity of 14, and 52 per cent an acidity of 15.

Generally speaking, the samples did not develop acidities near 20 at room temperatures (60° F.) until they had been kept for a day, and sometimes longer.

Our method of testing was as follows:—The freezing point and acidity were taken as soon as possible after drawing the sample. The remainder of the milk was loosely covered with a watch glass or clean piece of paraffined cardboard (milk bottle tops) and allowed to stand on the laboratory bench. At varying intervals afterwards, the bottles were shaken, a portion withdrawn, and the freezing point and acidity determined as before.

A Beckmann freezing-point apparatus was used, cooled by an ice and salt mixture, and fitted with a stirrer made from a piece of 12-gauge copper wire. The thermometer was graduated in 100ths of a degree Centigrade and could be read to half a graduation by inspection. The thermometer was checked repeatedly both with distilled water and cane sugar solutions.

The temperature of the ice and salt mixture was chosen to give a super-cooling of about -1.5°C. , as, contrary to the experience of other observers, we found that the best agreement between readings was obtained at this point. The mercury column would fall steadily to about -2°C. , then rise rapidly to a maximum, and then fall again slowly, the variation between readings seldom being more than approximately $\pm 0.002^{\circ}\text{C.}$ When the super-cooling was regulated to a lower degree, as recommended by Monier-Williams (*Food Report* No. 22), the results obtained were by no means so consistent. The portion to be tested was cooled in crushed ice, and when at a temperature of approximately 0°C. , it was poured into the containing vessel, and stirred steadily by hand, with an up-and-down movement, at the rate of about twice per second (four movements) during the whole time of the test.

The acidity was determined by titrating 17.6 c.c. of milk with $N/50$ sodium hydroxide solution, with phenolphthalein as indicator, when each c.c. of standard solution corresponds to 1 degree acidity; readings were taken to 0.5 degree.

To save space, the results are not tabulated here in detail, but in Fig. 1 are shown graphically the mean freezing points for different acidities (in circles), while for purposes of comparison the graph of $T = [C(A - A')] + t$ (with $C = 0.003$ and A prime = 20 degrees) is shown in dotted lines. The points are not plotted beyond an acidity of 65 degrees, as it was found that at acidities in excess of this figure the results were too erratic to have any practical value.

It will be noted that between 17 and 60 degrees acidity, a straight line could be drawn through the points, which would have a slope virtually the same as the dotted straight line of equation 1. Beyond 60 degrees the graph curves down rather steeply. Between 14 and 70 degrees, a straight line could also be drawn through the points without serious error, and by substituting 14 degrees instead of 20 for A prime in equation 1, and giving t a value of 0.545°C. and solving for C , a value of 0.010 is obtained.

With but one or two exceptions, all the above results were obtained from samples drawn from the cows received from farmers milking mixed herds, selected

after the usual analytical tests indicated that they were normal unadulterated milks. For purposes of comparison, several samples were taken from a herd of pedigree Jersey cows, and were found to behave in the same way as the other samples. Although it is an undoubted fact that some milks give abnormal results

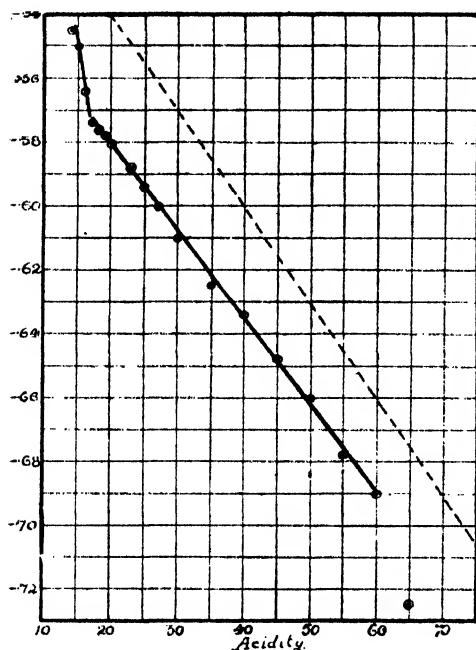


Fig. 1.

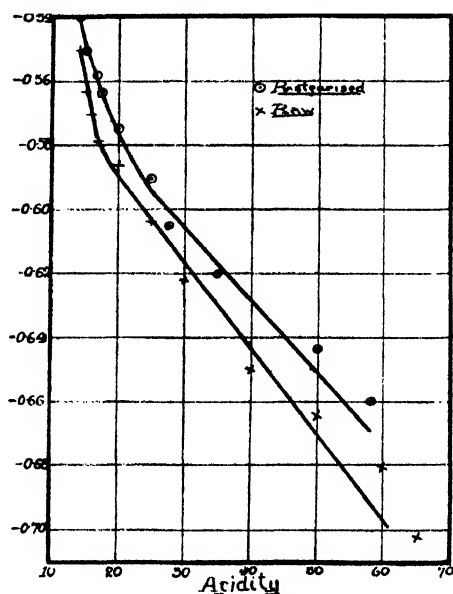


Fig. 2.

when subjected to the cryoscopic test, no such milks were encountered during the course of this investigation (this being due in all probability to the fact that the bulk of the work was on the mixed milks from herds of cows), although abnormal milks have occasionally been found in routine testing in this laboratory.

Having found in previous experiments that pasteurisation affected the freezing point, a series of experiments was made on milks before and after pasteurisation. A sample was drawn from the receiving vat of a local dairy factory, and a further sample was taken after pasteurisation, both samples being tested as previously described. The mean results of several determinations are shown graphically in Fig. 2. As a check on the results, a sample was drawn from the vat, taken to the laboratory, divided, and one portion pasteurised in a model pasteuriser made in the laboratory to imitate as closely as possible a "Cherry" pasteuriser, the heating coil being a glass spiral. The sample was heated rapidly by steam to 145° F., maintained at this temperature for 30 minutes, and cooled rapidly with cold brine to a temperature of 50° F. The raw and pasteurised milks were then tested. The results confirmed our previous experiments.

The effect of pasteurisation was to raise the freezing point by 0.01°C ., which in some cases would indicate "added water" in pure milk. The *A.O.A.C. Official Methods* (2nd Edition, p. 269), states that a tolerance of 3 per cent. of added water may be allowed on milk showing not more than 3 per cent. of added water, which is equivalent to a depression of 0.017°C .

Experiments were then made on milks to which distilled water was added, so as to give final products containing percentages of added water ranging from 2.5 per cent. to 40 per cent., and the same series of acidity and cryoscopic tests were repeated. In Fig. 3 the mean results are shown graphically for milks containing 5, 10, 20, and 40 per cent. of added water. It will be noticed that the

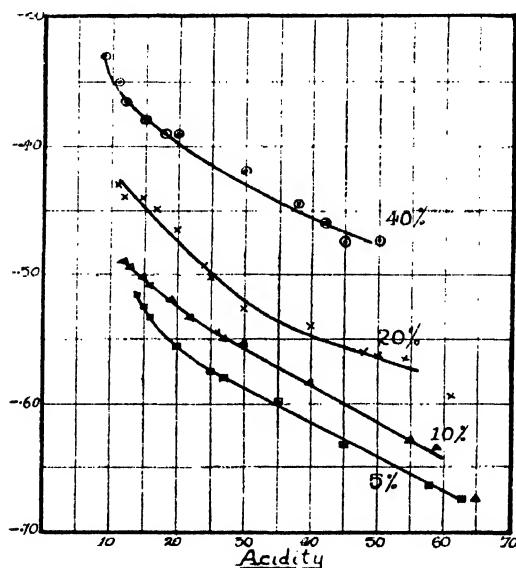


Fig. 3.

addition of the water lowers the original acidity of the fresh milk to a degree agreeing with calculated values. This is a factor which must be considered when applying a "correction" for acidity to samples which contain added water. Taking the 40 per cent. of added water curve as an example, it can be seen that the acidity of the first milk at a value of, say, 14 degrees, had been reduced by the dilution with water to an acidity of 9 degrees, and accordingly, any correction, to be of value, must be led back to this point. The error caused by calculating back to an acidity of 20 degrees would amount to approximately 11 per cent. of added water less than that which is actually present, which is a considerable error. Moreover, in our experiments, we failed to get results as consistent and reproducible with the high dilutions as with the low dilutions and with normal undiluted milks. Again, taking the 40 per cent., we found that results became most erratic when an acidity in excess of 50 degrees was reached, and this same feature was noted in all the diluted milks, becoming progressively less as the degree of dilution diminished.

The variations in the shapes of the different curves are to be noticed, the 10 per cent. curve being almost a straight line. The 5 per cent. curve shows some resemblance to the curve for normal milk, and could probably be drawn as two straight lines crossing at a point with co-ordinates approximately at 23 : 0.57°.

Auckland, New Zealand, being situated in a sub-tropical zone, the various experiments were carried out at times when the laboratory temperature was approximately 60° F., thus eliminating changes due to abnormal temperatures.

It might be mentioned that in the Auckland Province, dairy cattle remain outdoors in the grass pastures all the year round. During the winter, some of the cattle are provided with a wool-lined, waterproof rug.

SUMMARY.—Determinations of the variations of the freezing points of milk with increasing acidities have been made on a number of samples, both unadulterated and containing definite amounts of added water.

The value of 0.20 per cent. of acidity, given by the "Connecticut Agricultural Experiment Station, 27th Report on Food Products (1922)," as the normal acidity of fresh milk is criticised, and a value of 0.14 per cent. is suggested as being nearer the truth.

The correction factor of 0.003° C. for each 0.01 per cent. excess acidity is shown to hold between acidities of 0.17 per cent. and 0.60 per cent., and a value of 0.010° C. has been suggested for acidities ranging from 0.14 to 0.17 per cent. of lactic acid.

Results with milks containing added water are tabulated, which tend to show that when the cryoscopic method is used for the determination of added water in milk, it can be applied with accuracy only when the samples are quite fresh.

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DISCUSSION.

The PRESIDENT stated that this paper had come at a very opportune moment, when there was renewed interest in the analysis of milk and in methods of analysis which were not ordinarily applied, and there were signs that these would shortly be of increased importance. As far as this paper was concerned, he could not help regretting that fuller chemical analyses had not been made of some of the peculiar milks; it would be of importance and extreme interest to know the protein, lactose and ash contents, so that the relation of these factors to the freezing point factors could be studied. It would greatly increase the value of the paper if these details were given. He was surprised by the extraordinary constancy of the freezing point. So far as he had studied it, it always seemed that the freezing point, although the most constant property, was not nearly so constant as these results showed.

Dr. MONIER-WILLIAMS said that this was a most valuable paper. He could confirm the constancy of the freezing point of milk by work which he did in 1912 on a large number of samples, some of which were supplied by Capt. Golding, although his freezing points were rather higher than those given, *i.e.* -0.530° instead of

—0.550°. However, he noticed that the author's remarks as to the relative and not the absolute accuracy of the figures given rather disarmed criticism on this point. The real question was whether this method could be used in this country under the present system of administration. It appeared to be necessary that the milk should be "fresh," and generally it was not at all fresh when it arrived in the hands of the Public Analyst. This difficulty would be accentuated in the case of the third sample retained for eventual examination by the Government Chemist.

On the other hand, the constancy of the freezing point of milk appeared to him to open up considerable possibilities in the chemical analysis of milk. The freezing point was a measure of the osmotic pressure, and this depended on the relative proportions of the soluble constituents, chiefly lactose, chlorides, phosphates and citrates. In 1914 Mathieu and Ferré suggested a lactose-chlorine number for milk which they calculated from the percentages of lactose and chlorine, and which, they claimed, never fell below 74 for genuine milk. It might be possible by taking into consideration not only lactose and chlorine, but other soluble constituents, such as phosphates and citrates, to arrive at an expression which might show a degree of constancy of much the same order as that of the freezing point. The President, in his address to the Annual General Meeting, had made some very stimulating references to the need for research. Was not this problem an eminently suitable one for research? We knew really very little about the composition of milk. The analytical basis of the legal limit, depending upon the proportion of non-fatty solids, was admittedly crude. This figure represented the sum of a number of constituents which showed wide variation among themselves. The mutual variation of these different constituents must, however, be controlled by some natural law, or the osmotic pressure would not remain constant. It was for milk chemists to ascertain whether the results of chemical analysis could not be handled in such a way as to bring them more into line with the data afforded by the freezing point. The freezing point had been used on the Continent for the detection of added water for over thirty years, and the only attempt to apply the knowledge thus gained to chemical analysis was that of Mathieu and Ferré. He thought this was a matter which might well engage the attention of chemists in the future, and that such work might be of great value administratively. Later in the discussion Dr. Monier-Williams suggested that it might be worth while to ascertain the effect on the freezing point of adding thymol to milk, with the object of preventing the development of acidity.

Mr. H. T. CRANFIELD thought that this was certainly one of the most important papers concerning milk which the Society had received, in view of the fact that the problem of distinguishing between abnormal samples of milk and those containing added water was one which, in the near future, would demand very serious consideration. Dairy chemists, particularly those in direct touch with farmers, were brought right up against this problem repeatedly, and he thought that the method under discussion was one which showed promise of getting to the bottom of this difficulty. He agreed with the points that Dr. Monier Williams had brought forward, and, relative to these, he wished to state that in recent years determinations of the soluble ash in a number of these abnormal milks had been made in his laboratory. In the majority of cases, he had found that there was a strong negative correlation between the lactose and soluble ash percentages, but isolated samples gave figures which fell away considerably from the normal curve. One case under observation, that of an abnormal cow which produced milk of exceedingly poor quality, low in solids-not-fat, had yielded many interesting data. The results of the analysis of 250 samples of milk from this cow indicated that this correlation of lactose and soluble ash was, on the whole, quite good, but here again several samples did not follow the normal correlation curve. It was the presence of such samples which constituted the problem requiring solution.

He would like to suggest that if the Society were of the opinion that the "depression of freezing point" method was a promising one relative to our present difficulties, there was room for a very thorough investigation of the method in this country, but such an investigation would have to be on a large scale, dealing with thousands of samples. Personally he would warmly welcome the initiation of such a scheme.

The PRESIDENT here stated that with regard to his reference to abnormal samples he referred to those low in solids-not-fat content rather than those high in this respect.

Captain GOLDING said that he felt very strongly on this subject, and was greatly indebted to the Editor for asking him to read the paper. Since he had seen the paper he had made some tests by the method, and had compared it with the Hortvet test, which was official in America, and he was much impressed by the ease of the test. He suggested that instead of a Beckmann thermometer (with which, as the author stated, the zero point needed checking before and after each set of determinations) a Hortvet thermometer should be used. This was a very fine thermometer on which each degree was twice the length of those on the Beckmann thermometer, and there was no trouble in adjusting it. With regard to the point Dr. Monier-Williams had raised as to determining the other constituents of milk, it seemed to him that it would be comparatively laborious for the Public Analyst to make all those determinations, and, even then, there would be the question of decomposition of lactose, etc., whereas the freezing point was a fundamental and constant property of the milk. He had been very much impressed on reading the new book by Rogers to note the stress laid on the importance of this constant in fresh milk. Accurate determination of the freezing point, he said, would show whether there was added water, and surely if our methods for testing milk did not fit in with the present existing organisation, could not we alter the organisation? It seemed to him that it would be a very great help if there could be mobile laboratories where samples could be received, tested for freezing point, and fat determined by the Gerber method, and then the doubtful samples could be sent to the laboratory, where they could be fully analysed. This would mean that there would be no further cases of prosecutions of farmers who were unfortunate enough to possess cows which gave milk containing solids-not-fat below the average, and it would also detect the adding of water to rich milk. With reference to Dr. Monier-Williams' suggestion regarding thymol, Captain Golding thought it would be very interesting to investigate this point.

Mr. JEPHCOTT stated that he had the good fortune, when in New Zealand, to discuss this test with the author, and although he could see objections to the test from the point of view of the Public Analyst, it was of very great use in testing supplies of milk brought into the factories (where it was received approximately 2 hours after milking). He had never known it to fail, and in his own experience it had proved invaluable for detecting added water, often proving that quite a considerable amount of added water was occurring in milk which, considered from the point of view of fat and solids-not-fat, was satisfactory. Presence of added water was in every case confirmed at the farm.

The Use of Mixed Bromides in Place of Chlorides in the Determination of Alkalis.

BY E. SPENCER, Ph.D., F.I.C., A.R.S.M., AND
K. B. SEN, M.Sc., A.I.C.

INTRODUCTION.—It must have occurred to many analysts accustomed to routine determinations of potassium and sodium in rocks and refractory substances by the method of Lawrence Smith (*Amer. J. Sci.*, 1871, **50**, 269; *Chem. News*, 1871, **23**, 222) and that of Berzelius (*Pogg. Ann.*, 1824, **1**, 169), that the weighing of the two metals in the form of chlorides and the subsequent determination of sodium by difference, represents a weak link in these two methods. An error in the weight of the mixed chlorides, or in the potassium determination, involves an error in the sodium figure.

Some time ago, while carrying out a number of alkali determinations on felspar by the two methods above mentioned, it occurred to one of the authors that the substitution of ammonium bromide for ammonium chloride, and of hydrobromic acid for hydrochloric acid, in these determinations might lead to greater accuracy in the method, through yielding an increased weight of mixed halides.

Experiments were therefore made with the Lawrence Smith method thus modified. It was found that the rock decomposition could be effected at least as thoroughly with the bromide as with the chloride, and the resulting mixed alkali bromides were also found to be purer, less fusible, and less volatile than the corresponding chlorides. The weight of mixed alkali bromides is, of course, greater than that of the chlorides, by an amount depending on the proportion of potassium to sodium present, the increase varying from about 50 to 100 per cent.

It might be mentioned here that experiments were also carried out on the use of ammonium iodide and hydriodic acid as alternative halides, but, owing to the relative instability of hydriodic acid and its salts, consistent results could not be obtained, and these attempts were abandoned.

MODIFIED LAWRENCE SMITH METHOD.—A pure aqueous solution of hydrobromic acid was first prepared by distillation from potassium bromide and sulphuric acid. Similarly, pure ammonium bromide was prepared from hydrobromic acid and ammonia, the product being recrystallised. For the Lawrence Smith method 0.5 gm. of the dry ammonium bromide was intimately mixed with 0.5 gm. of the finely powdered mineral (as in the chloride method), and the mixture was then thoroughly incorporated with 3 grms. of precipitated calcium carbonate. About 0.5 gm. of calcium carbonate was placed in the platinum thimble, the assay mixture then transferred to the thimble, and another 0.5 gm. of carbonate placed on the top. The mixture was then heated in the usual way, after which the mass was lixiviated, as in the ordinary method, and the residue was treated with hydrobromic acid and found to dissolve completely.

The combined aqueous extracts were evaporated to a convenient volume, the excess of calcium precipitated with ammonia and ammonium carbonate, the filtrate evaporated to dryness, and ammonium salts removed by gentle heating. The residue was taken up in a little water, the last traces of calcium precipitated with a few drops of ammonium oxalate solution, and the precipitate filtered off. The filtrate was collected in a platinum dish and evaporated to dryness, the residue moistened with a little hydrobromic acid and again evaporated to dryness, and then heated to below a dull red heat for some time to drive off traces of ammonium bromide.

The resulting mixed alkali bromides were found to be whiter than the corresponding chlorides, owing, apparently, to the oxidising action of the hydrobromic acid or the ammonium bromide on the traces of organic matter usually present at this stage. The mixed bromides also appear to be less fusible than the chlorides.

After the mixed bromides had been weighed they were taken up in a little water and treated with 10 c.c. of perchloric acid, and the liquid was evaporated on the water bath until it fumed, diluted, and, after the addition of a further 2 c.c. of perchloric acid, again evaporated until fumes appeared. During the first evaporation the mass turned yellowish-brown, owing to the evolution of hydrobromic acid and its interaction with the perchloric acid. The second evaporation left the residue practically colourless. It was then cooled and taken up with about 30 c.c. of 97 per cent. ethyl alcohol, and the insoluble potassium perchlorate filtered off and weighed as in the ordinary perchlorate method.

MODIFIED BERZELIUS METHOD.—The success of this modification of the Lawrence Smith method suggested the application of the mixed bromide modification to the Berzelius method. In this method the alkalis are dissolved by means of sulphuric acid and hydrofluoric acid. After complete solution the liquid is heated to fuming to drive off free hydrofluoric acid, then cooled, the residue taken up in about 150 c.c. of hot water, and a slight excess of ammonia added to the solution to precipitate iron oxide and alumina. The precipitate is filtered off and well washed (if at all bulky it is reprecipitated). The combined filtrates are evaporated to dryness, and the residue heated below a dull red heat for some time to drive off the excess of ammonium sulphate.

The residue consists mainly of alkali sulphates, which in the Berzelius method are converted into the chlorides by adding a slight excess of barium chloride.

At this stage barium bromide was substituted for barium chloride, and, after the addition of a slight excess, the resulting barium sulphate was filtered off and well washed. The filtrates and washings were concentrated by evaporation, and the excess of barium (together with any calcium) precipitated with ammonia and ammonium carbonate. The filtrate and washings were evaporated to dryness in a platinum dish, the residue heated below a dull red heat to drive off the excess of ammonium bromide, cooled, again taken up in a little water, and any traces of barium or calcium precipitated with a little ammonia and ammonium oxalate and filtered off. The filtrate was finally evaporated to dryness in the platinum dish,

the residue moistened with a little hydrobromic acid, again evaporated to dryness, and heated to remove the last traces of ammonium salts. The mixed sodium and potassium bromides were then weighed and treated with perchloric acid, as in the Lawrence Smith method.*

DETERMINATION OF POTASSIUM AS PLATINIBROMIDE.—In using the above alternative method of weighing the alkalis as mixed bromides, one sacrifices the possibility of determining the potassium by the platinic chloride method. If, however, the alkali platinibromides show the same relative difference of solubilities that the platinichlorides do, it should be possible to determine the potassium in the mixed alkali bromides by the use of platinic bromide.

In order to examine this possibility platinic bromide was prepared (with difficulty) by dissolving precipitated platinum in hydrobromic acid and evaporating the solution to a syrup. The solubilities of sodium and potassium platinibromides were then determined in alcoholic solutions of various strengths, and it was found that ethyl alcohol of 90 per cent. strength gave a complete separation of the potassium and sodium salts. The following experimental tests with known weights of mixed alkali bromides illustrate the efficacy of the separation. The potassium platinibromide precipitate contains about 10 per cent. of potassium, as against about 16 per cent. in the platinichloride.

	Potassium bromide taken. Grm.	Sodium bromide taken. Grm.	Potassium oxide (calc.). Grm.	Potassium oxide found. Grm.
1.	0.005	0.0049	0.002	0.0029
2.	0.010	0.0049	0.0039	0.0039
3.	0.0250	0.0243	0.0099	0.0099
4.	0.0300	0.0292	0.0118	0.0120
5.	0.0350	0.0340	0.0138	0.0139
6.	0.0400	0.0389	0.0158	0.0159

CONCORDANCE OF RESULTS.—The following results of potassium and sodium determinations on rock substances of varying alkali content indicate the degree of concordance obtainable in the modified processes described in this paper:

METHOD.

Material.	Lawrence Smith method with chlorides and potassium pla- tinic chloride.		Lawrence Smith method with bromides and potassium perchlorate.		Berzelius method with bromides and potassium platinic bromide.
	Sodium oxide. Per Cent.	Potassium oxide. Per Cent.	Potassium oxide. Per Cent.	Potassium oxide. Per Cent.	Potassium oxide. Per Cent.
Moonstone felspar ..	4.75	9.59	9.61	9.68	9.68
Clinker	0.62	0.49	0.48	0.49	0.49
Fireclay	0.40	1.61	1.58	1.65	1.65

* The barium bromide for this experiment was prepared by dissolving pure baryta in a slight excess of hydrobromic acid solution.

Notes.

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

SANIO'S POTASSIUM DICHROMATE TEST FOR TANNINS.

O. HENRY (*J. prakt. Chem.*, 1834, 3, 7) was the first to suggest the use of potassium dichromate as a precipitant for tannins, especially gallotannin. His observations were confirmed by Wackenroder (quoted in Dekker, *Die Gerbstoffe*, 1913, p. 263), with the result that this reagent was accepted by Sanio (*Botan. Ztg.*, 1863, p. 17) as a specific test for tannins, and has since been extensively used in plant physiology, although it has been pointed out by Schroeder (*Jahr. Wiss. Bot.*, 1868, 7, 261), and by Drabble and Nierenstein (*Biochem. J.*, 1906, 2, 97), that gallic acid is also precipitated by potassium dichromate. In view of this, I have, at the suggestion of Dr. Nierenstein, investigated the matter, and have obtained the following results:

In accordance with Sanio's directions, saturated potassium dichromate was used. One c.c. of this solution, added to twenty-four different substances, in approximately 1 per cent. aqueous solution, precipitated gallic acid, gallotannin, pyrogallol, phloroglucinol, maclurin, cinchonine sulphate, and the hydrochlorides of berberine, quinine, strychnine, papaverine, narcotine and narceine. The remaining twelve substances, namely, β -resorcylic acid, veratric acid, salicylic acid, vanillic acid, oxalic acid, phenol, quercetin, rhamnetin, and the hydrochlorides of betaine, caffeine and pilocarpine, gave no precipitate.

In the case of the alkaloids, the precipitates obtained might possibly have been unchanged alkaloid hydrochlorides. The precipitate from berberine hydrochloride was therefore dried and ashed, when a distinct chromium ash was obtained.

It is necessary to point out that, although relatively concentrated solutions, compared with those existing in the plant, were used in this investigation, this is experimentally compensated for by the facts that precipitation occurs very much more easily on the cell wall than *in vitro*, and that plant precipitates are microscopical, compared with those obtained under laboratory conditions.

From these results, therefore, it is evident that no reliance whatever can be placed on the Sanio test for tannins.

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THE SOLUBILITY OF ANTIMONY IN WATER.

THE recent paper by S. G. Clarke (*ANALYST*, 1929, 99) sheds useful light on a subject in which I have been interested for some time past. The object of my experiments was to prepare a number of cathodic deposits by the electrolysis of certain neutral and alkaline solutions with an antimony cathode and platinum anode under varying conditions of electrolysis, and to compare their properties with those of the supposed hydride of antimony (Sb_2H_2) described by Weeks and

Druce (*J. Chem. Soc.*, 1925, 127, 1069). Such deposits are obtained under certain conditions as a finely divided black granular powder, adhering to the cathode, floating in the solution or settled on the bottom of the electrolysis vessel. As my experiments have shown (*ibid.*, 1928, 1987), the deposits obtained were in all cases metallic antimony containing a trace (about 0.1 per cent.) of hydrogen, and not antimony hydride, but the interesting point is that the principal property by which they could be distinguished from the hydride was their solubility in distilled water.

For example, when it was necessary to wash the deposits free from electrolyte with hot distilled water, for the purposes of analysis, a diminution in bulk of the deposit was visible to the naked eye. Even when the deposit was washed rapidly on a small Buchner funnel with cold distilled water, the washings were found to give a substantial precipitate with hydrogen sulphide.

As a result of further experiments it was found that solution of the antimony took place to a far less extent in the absence of air. Thus, when the electrolysis was carried out with a closed porous pot for cathode compartment in an atmosphere of hydrogen, the amount of deposit obtained was greatly increased.

Powdered antimony was found to have the same properties in this respect, though if the powder was freshly prepared the solubility in water was less marked but increased after exposure to air.

It appears therefore, that metallic antimony in a finely divided state is soluble in distilled water in the presence of oxygen owing, probably, to oxidation. Under certain conditions this may prove an appreciable source of error not only in Clarke's method, but also in other analytical operations where deposits of antimony (produced, for example, electrolytically) have to be washed. (*Cf. Schoeller, J. Soc. Chem. Ind.*, 1913, 32, 260.)

JULIUS GRANT.

THE DETECTION, DETERMINATION AND OXIDATION OF SULPHUR DIOXIDE.

THE apparatus shown in the accompanying diagrams has been designed with the intention of combining the rapidity of the method of the Manufacturing Confectioners' Alliance and of the Food Manufacturers' Federation (*ANALYST*, 1928, 53, 118) with the accuracy of the Monier-Williams method (*ANALYST*, 1927, 52, 343, 515).*

Qualitative Test for Sulphur Dioxide by means of Apparatus A.—It will be seen that the apparatus consists of two bulbs, the lower one of which prevents any liquid being drawn back into the flask, and also acts as an absorption bulb, while the upper bulb contains the bulk of the liquid by which the sulphur dioxide is absorbed.

Ten ml. of hydrogen peroxide are placed in the lower bulb, two drops of bromphenol blue added, followed by *N*/10 sodium hydroxide solution until the liquid is just blue, and the vent is closed with a small rubber stopper. The apparatus is then fitted by means of a rubber stopper into the top of a reflux condenser, and a 500 ml.-flask, containing 150 ml. of air-free water, is fitted to the bottom of the condenser by means of a rubber stopper, through which passes a glass tube connected with a cylinder of carbon dioxide; the flask is supported by wire gauze. Carbon dioxide is then passed through the apparatus to expel air, and

* The apparatus was made by the Scientific Glass-blowing Co., 95, Gray's Inn Road, London, W.C.1.

most of the hydrogen peroxide is brought into the top bulb, leaving one or two ml. in the lower bulb. A weighed quantity of the sample is placed in the flask, followed by 50 ml. of a 16 per cent. (by volume) solution of hydrochloric acid, and the flask is then heated over a Bunsen flame. If a considerable quantity of sulphur dioxide is present, the indicator in the lower bulb will change to yellow before the liquid in the flask has reached the boiling point. (The indicator is not, by itself, reduced by sulphur dioxide.) In the presence of traces of sulphur dioxide the liquid in the lower bulb will show the colour change within 5 minutes from the commencement of boiling.

A series of qualitative tests for the presence of sulphur dioxide may be made in a very short time by this method. If a positive result is obtained, the amount is determined by continuing as follows:—

Quantitative Test for Sulphur Dioxide by means of Apparatus A.—It was found that the sulphur dioxide was entirely absorbed by the liquid in the two bulbs.

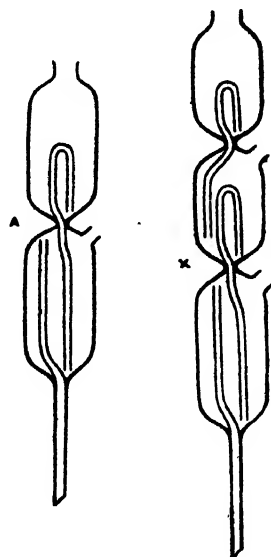
The change of colour of the indicator in the lower bulb is followed by a colour change in the upper bulb. The liquid in the upper bulb is then titrated with $N/10$ sodium hydroxide solution as the test proceeds. When the neutral point is reached the liquids in the bulbs are mixed by manipulating the supply of carbon dioxide, and again titrated, etc., until the final neutral point is reached. The flow of water through the condenser is now stopped, and heating continued until the neck of the condenser is hot. The liquids are then finally titrated.

To guard against any sudden evolution of gas, the neck of the bulb may be fitted with a splash-tube, which consists of a short piece of wide-bore tubing containing a small bulb and inclined at an angle. In order that the tube may be as wide as possible, a small piece of rubber tubing is used as a stopper, but with a steady flow of gas this fitting is not necessary.

The bulbs of the inner jacket of the condenser should not touch the outer jacket, as condensed water collects at these points, and the sulphur dioxide retained may not be entirely driven out when the condenser water is heated at the end of the test. Moreover, a condenser which allows a wide passage from the flask to the absorption bulbs may cause traces of chlorides to be carried through; for this reason diluted hydrochloric acid is added in the proportions previously given, to avoid any possibility of fumes being carried up to the bulbs, as might occur if strong acid were added just before distillation.

A blank test is advisable, and for this purpose distilled water containing two drops of the indicator is placed in the bulbs. (The indicator turns blue with distilled water, as the P_H figures for bromphenol blue range from 3.0 to 4.7.) Carbon dioxide is then passed through the boiling hydrochloric acid solution, and no change should take place in the indicator.

The following comparative results were obtained in test experiments, in which 10 ml. of a freshly made aqueous solution of sulphur dioxide were taken in every case, the strength of the solution being determined by titration with $N/10$ sodium hydroxide solution after oxidation with neutral peroxide. The time taken for



each test varied from about 20 to 30 minutes, including the time taken to heat the liquid to the boiling point.

	Sulphur dioxide added.		Sulphur dioxide found.
	By titration after oxidation with H_2O_2 $N/10$ NaOH. Ml.	By titration $N/10$ Iodine. Ml.	By titration $N/10$ NaOH. Ml.
Apparatus A	10.40	10.45	10.35
	10.20	10.15	10.20
	15.0	14.95	14.80
	13.05	13.05	12.90
	12.95	12.85	12.70
Apparatus X	13.05	—	12.6
	13.3	—	12.9
Method of <i>Monier-Williams</i> *	31.9	31.7	31.2
	14.8	14.4	14.3
	10.3	10.4	9.9
	6.3	6.4	6.1

* These figures are calculated from mgrms. of sulphur dioxide shown in the table on page 44 of his Report.

It will be seen that the use of the apparatus A affords a rapid qualitative and quantitative method of determining sulphur dioxide.

Quantitative Determination by means of Apparatus X.—This apparatus was designed with an extra bulb, so as to make certain that no sulphur dioxide could escape.

Fifteen ml. of neutralised hydrogen peroxide are placed in the lower bulb, and the vents in the two bulbs closed with rubber stoppers. The length of the tube in the centre bulb is such that when carbon dioxide is passed through it and the peroxide is raised into the bulbs 10 ml. will remain in the centre bulb and the remainder will pass into the upper bulb. The peroxide may be titrated during or at the end of the determination.

The Oxidation of Sulphur Dioxide.—As mentioned by Monier-Williams in his Report, Cazenave and Claassen considered the use of carbon dioxide unnecessary. Froboese stated that an atmosphere of carbon dioxide is not so important as the use of air-free water in the distilling flask, and that the carbon dioxide does not prevent oxidation, but merely assists in carrying over the sulphur dioxide. Raschig states that when titrating by running iodine into sulphurous acid the errors observed are due solely to the escape of sulphur dioxide from the liquid during titration. This was confirmed by Mason and Walsh (*ANALYST*, 1928, 53, 144) using sulphite solutions, and in this case the loss, though mainly due to volatilisation, is partly due to oxidation of the *sulphite*. The use of glycerin by Brown to prevent oxidation resulted probably in checking, to a great extent, the loss by volatilisation. The loss of sulphur dioxide obtained by many chemists has been shown to be mainly due to volatilisation.

In the early experiments with the apparatus which has been described sulphite solutions were used, but the oxidation was so rapid that these were discarded and solutions of sulphur dioxide in air-free water were used. Although these solutions lost strength slowly, the loss was due to volatilisation and not to oxidation. This

was proved by means of iodine titrations made at the same time as the titration with alkali after oxidation.

A series of experimental determinations with tap water and air has shown that sulphur dioxide itself is not appreciably oxidised, at any rate during the period of the test, the determinations being quite as accurate as when air-free water and carbon dioxide were used. In a test with jam, 50 grms. of the sample (from the same quantity of which 0.5 ml. *N*/10 sodium hydroxide had been required by the Monier-Williams method 5 days previously) were placed in tap water, diluted acid added, and air blown through. 0.4 ml. of *N*/10 sodium hydroxide solution were required. Sulphur dioxide in combination with aldehydes and sugars is not readily oxidised, which fact may explain this result.

These, and other experiments, proved that the loss of sulphur dioxide is not due to oxidation but to volatilisation, and that more sulphur dioxide is lost during the mixture of the sample, weighing out, and introduction into the flask than in the actual determination. Inaccuracies in the determination of sulphur dioxide in past experiments have been due, firstly, to the interference of volatile acids, sulphur-containing substances, etc. (this interference is now prevented in the Monier-Williams method); and secondly, to the difficulties in sampling, with loss of sulphur dioxide by volatilisation and of sulphur dioxide as sulphites, etc., by oxidation.

Mr. E. Hinks (ANALYST, 1928, 53, 128) expressed the opinion "that oxidation really took place in solution rather than in the gaseous state."

The experiments which have been described show that neither in solution nor in the gaseous state, during the time of the experiment, is sulphur dioxide (*as distinct from sulphites, etc.*) appreciably oxidised.

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Notes from the Reports of Public Analysts.

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

COUNTY OF SOMERSET.

ANNUAL REPORT OF THE COUNTY ANALYST AND BACTERIOLOGIST FOR 1928.

THE total number of samples examined was 11,652, of which 1072 were taken under the Sale of Food and Drugs Acts. Of the 1043 samples submitted by the police, 1010 were genuine, 8 suspicious, and 25 adulterated.

MILK SAMPLES EXAMINED FOR TUBERCLE BACILLI.—Of 391 samples examined, 26 were found to contain tubercle bacilli. Systematic examination of the milk from the herds of the County have been made, and, as before, about 2 per cent. have been found to contain tubercle bacilli. When a tuberculous herd has been found, the infecting cow or cows are tracked down, veterinary surgeons send samples from suspected cows, and the herd is sometimes sampled in small groups.

During the year six herds, A, B, C, D, E, and F were found in this laboratory to give tuberculous milk, and in the Bristol Laboratory one herd, G. Five cows, and a small group of 4 cows (under investigation), giving tuberculous milk, were discovered—one in herd A, one in herd B, two in herd C, and two in the herd G supplying Bristol. One infecting cow, which had gone dry, was discovered by the veterinary surgeon in herd D. In herds E and F no infecting cow was found, but further investigations are being made. In five out of the six herds veterinary inspection was insufficient to discover the infecting cow. Apart from the examination of milk from herds, animals are inspected by veterinary surgeons and samples of milk are sent under the provisions of the Diseases of Animals Act.

DENYS R. WOOD.

Legal Notes.

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

STANDARD FOR WATER IN MARGARINE.

ON January 31st a grocer was summoned at Southampton for selling, to the prejudice of the purchaser, margarine containing an excess of moisture.

On analysis, the sample was found to contain: Water, 17·43; fat, 80·10; salt, 2·34; and curd, 0·13 per cent.

The solicitor for the prosecution explained that there was no legal standard for water in margarine when sold, although there was a standard under the Butter and Margarine Act, 1907. Sec. 4 of the Sale of Food and Drugs Act stated that if any margarine prepared for sale or consignment contained more than 16 per cent. of water, and was present in any margarine factory, it should be an offence, but there was no offence under the Act for selling the article, so that the prosecution had to fall back upon the Act of 1875, which made it an offence to sell any article to the prejudice of the purchaser. The authority was the case of *Burton v. Mattison*, in which it was held that the sale of margarine containing 21 per cent. of moisture was an offence under Sec. 6 of the Food and Drugs Act.

For the defence it was urged that the excess of moisture was due to the margarine being beaten with wet beaters, but that, as the beating took place after the margarine was weighed, the customer obtained full weight. That, however, was not the point, for the question was, what amount of moisture was present. Although there was no fixed standard, this was not relied upon by the defence, because prior to the Butter and Margarine Act of 1907 the Magistrates had made their own standard. The defendant had bought the margarine under a warranty, which required him to sell the article as received, but as it was sliced off the bulk and beaten on the block, it was not sold as received, and therefore defendant did not rely on the warranty.

A fine of 10s. was imposed.

Department of Scientific and Industrial Research.

FUEL RESEARCH. Technical Paper No. 21.

THE ASSAY OF COAL FOR CARBONISATION PURPOSES (PART II).*

CONTINUED experience with the Gray-King apparatus, designed to obtain reliable data as to the suitability of coal for carbonisation, has shown its value, but for strongly swelling coals it is necessary to mix the air-dried coal with air-dried coke or electrode carbon, so that the swelling of 20 grms. of the mixture does not fill the cross-section of the retort tube, and the coal is thus not projected beyond the zone of uniform heating. Correlation of the assay method with low temperature carbonisation on a larger scale may be made to give information as to the yield of products (tar, condensable spirit and gas) and caking power. Many experimental data are given, and two plates showing different assay cokes produced from various types of coals.

Appendix I is reprinted from Methods of Analysis of Coal. Physical and Chemical Survey of the National Coal Resources No. 7 (ANALYST, 1927, 52, 594), and describes the Gray-King Assay of Coal.

Appendix II comprises notes on manipulation. The furnace should be so wound and lagged that the temperature gradient towards the end is not too great, and so that the centre 6 in. (at least) of the tube is at uniform temperature. It is most important that the layer of coal should be of uniform depth and 6 in. in length. Acetone is suitable for removing the film of tar from the end of the retort tube, but the tube should be so clamped that no solvent reaches the coke, and vapour should be gently blown out. A small wad of asbestos wool should be used with coals showing a tendency to form a tar fog. In order to determine the composition and density of the gas, duplicate experiments may be run and the gases from the second swept backwards through the absorption train to remove air, or, alternatively, the amount of oxygen may be determined and a correction made. To obviate the difficulty of gas of different composition in the train and holder, a gas reservoir may be attached and the gas mixed by circulation. The effect of excluding the gas in the train is an increase of 0.02 on a density of 0.64, *i.e.* 0.25 per cent. of the coal. A distillation apparatus for determining the water of distillation is illustrated; it gives results accurate to within 0.02 c.c. In the standard assay, coal dried at 105° C. is used, and the water is therefore water of distillation, less that carried forward in the gas, and the latter is negligible with condenser water at 15° C.; but when air-dried coal is used the water collected is the sum of water of distillation, and the moisture, as determined by drying at 105° C. Uncondensed liquid hydrocarbons may be determined by absorption in activated charcoal or condensation in liquid air after passing the gases through a drying tube and removing carbon dioxide.

Appendix III deals with large scale Low Temperature Assay. A diagram is given of the apparatus. A cylindrical retort (15 in. long by 4 in. internal diameter) with an inset thermometer, has a cover with a baffle plate, 8 in. within

* By J. G. King, C. Tasker, and L. G. Edgcombe. H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 1s. net.

the retort, with a 1 in. off-take pipe inclined at 45° and fitted with an iron condenser 3 in. long, cooling sufficiently to allow of a rubber joint from the off-take pipe to the first condenser. This is connected with a second condenser by a side tube, and at its lower end with a seal pot. The second condenser is packed with contact rings and has a side manometer and loose plugs of asbestos. Ammonia is removed by 2 wash bottles charged with 40 per cent. sulphuric acid, and a glass scrubber removes light spirit from the gas. The coal is crushed to pass a 10-mesh I.M.M. sieve and air dried, and the condensing system with seal pot are weighed, and about 50 grm. of water weighed into the seal pot. Five hundred grms. of coal are weighed, and the retort placed in the furnace previously heated to 500°C . The temperature of the coal is raised to 300°C . in 20 minutes, and from 300° – 600° in 1 hour, and kept at this temperature for 40 minutes. The pressure in the manometer is maintained at level gauge by adjusting the weights in the gas holder. Preliminary separation of the tar and liquor can be effected during carbonisation by changing the receiver to the overflow of the seal pot. After draining for 30 minutes, the condensing system is weighed and the increase counted as tar. The tar and liquor are weighed, separated, and the liquor in the wet tar obtained by distillation. When cold, the coke is removed and weighed. Typical results are given for Dalton Main Coal.

Appendix IV is a reprint of Gray-King assays of a range of coals.

D. G. H.

MANUFACTURE, USE AND STORAGE OF CELLULOSE SOLUTIONS.*

THE principal liquids used in the manufacture of cellulose solutions are: (I) Fatty esters, such as amyl, butyl, propyl and ethyl acetates; (II) Higher esters of the corresponding alcohols, such as amyl tartrate and ethyl lactate; (III) True ketones, particularly acetone, and mixed ketones of which methyl ethyl ketone is typical; (IV) Methylated spirit, wood spirit, variable mixtures of the higher homologues of ethyl alcohol known as fusel oil, and butyl alcohol; (V) Coal tar hydrocarbons, principally benzene (90 per cent. benzol) and its homologues; (VI) Dibutyl phthalate, diamyl phthalate and tricresyl phosphate; (VII) Flexible oils, principally castor, rape-seed and linseed oils.

The most valuable solvents are amyl, butyl and ethyl acetate, and particularly ethyl lactate, but owing to high price these are diluted with cheaper ones. Usually the makers supply thick solutions and a stock of mixed solvents as thinnings. As the solvent is the vehicle for conveyance of the solids to the surfaces to be treated, drying takes place by evaporation of those solvents, which gives rise to special dangers.

The recommendations of the Report are mainly concerned with the importance of ventilation and avoidance of fire. It is suggested that all articles should be treated in cabinets or enclosures of fire-resisting construction, enclosed on 3 sides, with properly designed mechanical ventilating appliances, such that the inward air velocity through the working opening of the cabinet should be at least 75 linear feet per minute, or in a room the air should be renewed at least 30 times an hour. Direct fan discharge should be used and ducts avoided. All parts where residues may accumulate should be frequently cleaned with non-ferrous implements. No flame or other agency capable of igniting the mixtures of air and vapour should be

* Factory Dept., Home Office. Form 826. Obtainable at H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 3d. net.

permitted in or near the workrooms, particular care being taken of all electric installations, with bonding to earth of all metal pipe lines, metal parts of mixers, etc. Storing of bulk solutions needs great care, and where the flash point is below 73° F. a license under the Petroleum Act is necessary. No stocks beyond the day's requirements should be kept in the work rooms, and these, as far as possible, in metal cupboards. Floors should be impermeable to vapours. Adequate means of escape from the buildings is required, with appliances for fighting fires, and in all cases of making and adapting premises the advice of the District Factory Inspector should be sought.

D. G. H.

Ministry of Health.

BACTERIOLOGICAL TESTS FOR GRADED MILK.*

STANDARDS.

1. The following bacteriological standards for the various classes of graded milk are prescribed by the Milk (Special Designations) Order, 1923:—

CERTIFIED MILK AND GRADE A. MILK PASTEURISED.	The milk must not contain more than 30,000 organisms per c.c. and must not contain coliform bacillus in 1/10 c.c.
GRADE A. (TUBERCULIN TESTED) MILK AND GRADE A. MILK PASTEURISED MILK.	The milk must not contain more than 200,000 organisms per c.c. and must not contain coliform bacillus in 1/100 c.c. The milk must not contain more than 100,000 organisms per c.c.

SAMPLING.

2. Where the milk to be sampled is contained in bottles each sample should consist of one bottle (with seal unbroken) taken anywhere between the place of bottling and the consumer. Where the milk to be sampled is not contained in bottles, samples should be taken and despatched in specially sterilised four-ounce or six-ounce bottles, each bottle being properly fastened and sealed.

3. On collection the bottles must be transferred forthwith to a carrying-case and well packed in ice, and must be kept in this condition until plated at the laboratory. (This precaution may be dispensed with only if the bacteriologist considers it unnecessary on account of the proximity of the laboratory to the place in which the samples are collected.)

4. If the plates are not made within 30 hours of the time of milking, or in the case of pasteurised milk, of the time of pasteurisation, the additional time must be stated on the report, and in any case must not exceed 12 hours.

LABORATORY TECHNIQUE.

5. In order that the results obtained by different bacteriologists engaged in the examination of official samples of graded milk may be comparable, the adoption of a strictly uniform technique is highly desirable. The technique described below has been found to be satisfactory, and should for this reason be universally adopted.

MEDIUM FOR PLATES.

6. To prepare the medium take—

1,000 c.c.	Tap water.
5 grms.	Peptone.
3 grms.	Lemco.

* Memo. 139/Foods. H.M. Stationery Office, Kingsway, W.C.2. Price 1d. net.

7. Dissolve by heat and filter hot through paper, add 15 grms. agar (best quality, clean); dissolve by heat, titrate with phenolphthalein. The reaction will usually fall between +5 and +10 on Eyre's scale, and the medium may then be used without any further adjustment of titre. If a batch does not fall within these limits, it should be brought within them by adding the minimum amount of acid or alkali.

8. Cool to 45° C., then bring to boiling point and filter through paper or absorbent cotton until clear. Eggs must not be used for clearing.

9. Distribute in flasks and sterilise for 30 minutes in 15 lb. pressure, or for 20 minutes on three successive days in the Koch steriliser.

DILUTIONS.

10. Dilutions of (a) $\frac{1}{10}$, (b) $\frac{1}{100}$ and (c) $\frac{1}{1000}$ should be made in bottles containing accurately measured quantities of sterile water and fitted with glass stoppers; or by some other means which makes shaking possible. The dilution should be:—

- (a) 90 c.c. water plus 10 c.c. milk;
- (b) 90 c.c. water plus 10 c.c. of the (a) dilution;
- (c) 90 c.c. water plus 10 c.c. of the (b) dilution.

11. At least two pipettes are required for each sample, one for dilution (a), another for dilutions (b) and (c); the latter pipette should be washed out ten times in each dilution as it is made. Alternatively, a separate pipette may be used for each dilution. Straight-sided pipettes (not bulbed) should be used.

12. In making dilutions the original sample and each dilution bottle must be shaken 25 times, each shake being an up-and-down motion, with an excursion of about one foot.

In making the plate, put the required quantity of diluted milk into a sterile tube (5 in. by 1 in.) and add about 15 c.c. of melted agar cooled to 45° C.; then pour the mixture into a Petri dish (3½ ins. internal diameter). The depth of the agar in each Petri dish should be uniform.

13. Not more than half an hour should elapse between the dilution of the milk and the pouring of the plate.

14. After the agar has thoroughly hardened, incubate for 48 hours at 37° C.

COUNTING OF COLONIES.

15. If among the different dilutions there are plates containing from 30 to 300 colonies, these should all be counted, and the number, multiplied by the dilution, reported as the final count. If there are no plates within these limits, that which comes nearest to 300 should be counted. No plate that contains less than 20 colonies should be counted, unless there are no plates with a larger number. If the number of colonies on a plate is over 300, a part of the plate may be counted and the whole plate averaged.

"COLI" TESTS.

16. For Certified milk and Grade A. milk Pasteurised, three tubes, each containing 10 c.c. of bile-salt lactose peptone water,* and a Durham's fermentation tube, should be inoculated each with 1/10 c.c. of the sample under examination, and incubated at 37° C. For Grade A. (Tuberculin Tested) and Grade A. milk, three tubes should each be inoculated with 1/100 c.c. of the milk.

17. An uninoculated control tube should also be incubated.

18. The tubes should be examined for acid and gas production at the end of 48 hours. The milk is regarded as satisfactory in respect of this test if two out of the three tubes are found to be free from acid plus gas after 48 hours' incubation.

REPORTS.

19. The results of both bacteriological examinations should be recorded on a form similar to that contained in the Appendix to this Memorandum, and the report should be sent to the Ministry or the Licensing Authority immediately on the completion of the examination.

MINISTRY OF HEALTH,

WHITEHALL, S.W.1.

February, 1929.

* This should be prepared as follows:—Five grammes each of sodium taurocholate and lactose, 20 grammes of peptone, and 1 litre of water are heated together until the solids are dissolved. The mixture is filtered and sufficient strong neutral litmus solution is added to give a distinct colour. The medium is then distributed into fermentation tubes, and sterilised by steaming for 20 minutes on three successive days.

APPENDIX.

MILK (SPECIAL DESIGNATIONS) ORDER, 1923.

REPORT OF BACTERIOLOGICAL EXAMINATION OF.....*MILK.

Name and Address of Producer:
 Date and Time of Production:
 Name and Address of Dealer:
 Date and Time of arrival at Dealer's Premises:
 Place where sample taken:
 Date and Time sample taken:
 Quantity of sample.
 Date and Time of { delivery at } Laboratory:
 { dispatch to }
 Signature of Inspector obtaining sample:

BACTERIOLOGIST'S REPORT.

No. of sample:
 Age of sample when received.....hours.
 Temperature on arrival:
 Number of Bacteria per 1 c.c.:
 Presence or absence of Coliform Bacillus in† c.c. (in each of three tubes) after 48 hours' incubation:
 Tube 1.
 Tube 2.
 Tube 3.

REMARKS.

CONCLUSION.—I am of opinion that the sample { complied
 { did not comply } with the prescribed
 conditions.

Signature.

Name and address of Laboratory.

Date.

* Insert designation, i.e. "Certified," &c.

† Insert 1/10 or 1/100 according to grade of milk (*see* instructions).

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Tests for the Degree of Heating of Milk. P. Weinstein. (*Z. Unters. Lebensm.*, 1928, 56, 457-467.)—The following are the author's methods of applying the more important tests to obtain an indication of the extent to which milk has been heated. *Schardinger's test*.—Ten c.c. of milk and 1 c.c. of a mixture of 5 c.c. of a saturated alcoholic solution of methylene blue, 5 c.c. of 40 per cent. formaldehyde solution and 190 c.c. of water, are maintained at 40 to 45° C., and the time to produce complete decolorisation noted. Raw milk requires 5 to 10 minutes.

Catalase test.—The oxygen liberated from 15 c.c. of milk and 5 c.c. of a 1 per cent. solution of hydrogen peroxide after 2 hours at 22 to 25° C. is determined, a normal value being 30 to 50 c.c. per 100 c.c. of milk. **Amylase test.**—A series of test tubes containing 10 c.c. of milk and 0.1 to 0.9 c.c. of a 1 per cent. solution of starch is heated at 37° C. for 50 to 60 minutes, cooled, and 3 c.c. of a solution of 1 grm. of iodine and 2 grms. of potassium iodide in 300 c.c. of water added. The mixtures are coagulated with 5 c.c. of 5 per cent. acetic acid, filtered, and the colours of the filtrates, which vary from yellow to violet-blue, according to the amount of unchanged starch, are compared after dilution to 100 c.c. **Skim test.**—A mixture of 48 c.c. of milk and 0.15 c.c. of a saturated alcoholic solution of alkali blue-6B is heated for 90 minutes at 45 to 50° C. in a graduated cylinder, and the height and colour of the fat layer noted after 30 minutes, at 15-minute intervals. The colour, which depends on the lactic acid present, is pale blue for raw milk. The Rothenfusser-Storch oxydase test was also used. Experiments with raw milks and milks heated under varying conditions of time and temperature showed that milk pasteurised at 85° C. for 1 minute gave no Storch reaction. After 30 minutes at 70° C., however, the reaction was positive, though no decolorisation was produced in the Schardinger test within 22 minutes. Well-sterilised milk gave a positive Storch reaction, decolorised Schardinger's reagent within 10 minutes, and had the low catalase value of 9 c.c. of oxygen per 100 c.c. Insufficiently sterilised milk had a catalase value of more than 10, and a positive amylase reaction. Milk heated at 55° C. or less had an amylase value of 0.1 to 0.5 c.c. of starch, and the catalase value of normal milk, and gave a light blue fat layer in the skim test. Mixtures of raw and heated milks gave a strongly positive amylase reaction, and a bright blue fat layer, the other properties being dependent on the proportions of the mixture.

J. G.

Albuminous Compounds from the Meat of Different Animals. K. Beck and E. Casper. (*Z. Unters. Lebensm.*, 1928, **56**, 437-457.)—Striegel's method (*Chem. Ztg.*, 1917, **41**, 313) was used for the separation of glucose, a 2 per cent. solution of the sample being coagulated by heating under a reflux condenser for 5 hours, and then for a further 30 minutes after the addition of 1 per cent. of tartaric acid. The clear solution was neutralised with sodium hydroxide solution, the albumoses removed by precipitation with 10 per cent. of a saturated solution of zinc sulphate, and the glucose finally obtained by the addition of a solution of 22.5 grms. of nitrogen-free tannin and 9 grms. of acetic acid in 100 c.c. of water. Van Slyke's phosphotungstic acid method, as described by Abderhalden (*Handbuch der Biochemischen Arbeitsmethoden*, 1912, p. 1011), was used for the determination of the various nitrogen compounds obtained after hydrolysis of the sample or of the glutin-tannin precipitate for 5 hours at 135° C. with 6 times the amount of 20 per cent. hydrochloric acid, the excess of acid being finally removed *in vacuo* and the solution diluted with water. The distribution of the nitrogen was then calculated from Van Slyke's formulae (*loc. cit.*), non-amino $N = (\frac{1}{3} \text{ arginine } N + \frac{2}{3} \text{ histidine } N)$, and lysine $N = \text{total } N \text{ of the bases (arginine } N + \text{histidine } N)$. The total nitrogen

was determined by Kjeldahl's method. The results lead to the main conclusion that there is a close relationship between the distribution of nitrogen in the glucose obtained from edible gelatin and from a Liebig's meat extract, and a common origin is suggested. Examination by similar methods of the hydrolysis products of muscular fibres of the ox, calf, pig, sheep, horse, goose and cod previously freed from fat, washed, dried and powdered, gave figures which were similar in all cases, and therefore cannot be used as a guide to the origin of a particular product. Extracts of the meat of the above animals were also examined, the total nitrogen, albumoses and glucose being obtained by the above methods, while, in addition, amino-acid nitrogen was determined gasometrically by means of nitrosyl chloride, the creatinine by Folin's colorimetric method, and the total phosphorus by titration of a solution of the ash. The results, which are tabulated, show wide variations, the extract from the cod, in particular, being high in coagulable nitrogen, albumoses and glucose, but low in creatinine, phosphorus and amino-acid nitrogen. Horse and pig's flesh gave extracts low in glucose. J. G.

Determination of Traces of Iodine in Vegetables. J. F. McClendon and R. E. Remington. (*J. Amer. Chem. Soc.*, 1929, 51, 394-399.)—Five kilos. of the fresh vegetables are ground, dried, and formed into rods about 50 mm. long and 24 mm. in diameter. These rods are placed in a steel tube fitted with a screw piston by which they are forced slowly into a combustion tube where they are burned in a current of oxygen. The other end of the combustion tube connects with a series of absorption vessels containing sodium hydroxide solution, and these in turn connect with a Cottrell precipitator and an air pump. When the combustion is completed, the ash in the combustion tube is removed, ground, extracted with water, and the solution added to the evaporated contents of the absorption vessels and precipitation vessel. The whole is then evaporated, the residue heated in a nickel boat in a Pyrex combustion tube, the ash is dissolved in sodium hydroxide solution, acidified with a mixture of phosphoric acid and sulphurous acid, boiled to expel sulphur dioxide, and rendered acid to bromphenol blue paper by the addition of a few drops of sulphuric acid. The solution is treated with a small crystal of sodium nitrite, carbon tetrachloride is added, and the liberated iodine is determined colorimetrically. An alternative method consists in igniting the sample, previously moistened with calcium lactate and sodium carbonate solution, at a temperature not exceeding 450° C. until the ash is light grey in colour, and then proceeding as described. W. P. S.

Isolation of Mesaconic Acid from Cabbage Leaves. H. W. Buston. (*Biochem. J.*, 1928, 22, 1523-1525.)—The isolation of mesaconic acid from the products extracted from green leaves (cabbage) was mentioned by Buston and Schryver (*Biochem. J.*, 1923, 17, 470), and a more detailed account of its discovery is now given. From 90 kilos. of fresh leaves 6.0 grms. of acid were obtained (5.0 grms. of recrystallised product from the "dicarboxylate" fraction and 1.0 gm. from the "organic phosphate" fraction). Mesaconic acid, $C_6H_4(COOH)_2$, is an unsaturated dicarboxylic acid, with a molecular weight of 130, and m.pt. of 202° C.

The 6 grms. obtained must not be regarded as the total amount present, as the methods of separation were by no means quantitative. Mesaconic acid has not previously been met with as a naturally occurring product. It may be connected with citric acid, which with loss of water gives aconitic acid, and this with loss of carbon dioxide gives citraconic acid, the optical isomer of mesaconic acid. The change from citraconic acid to mesaconic acid is not easily explained; however, mesaconic acid appears to be present as such in the leaf.

P. H. P.

Isolation of Protocatechuic Acid from Pigmented Onion Scales.

K. P. Link, H. R. Angell and J. C. Walker. (*J. Biol. Chem.*, 1929, **81**, 369-375.)—Protocatechuic acid (3, 4-dihydroxybenzoic acid) has been isolated from pigmented onion scales. This phenolic acid appears to be one of a group of toxic substances that enable the pigmented onions to resist the inroads of the fungus, *Colletotrichum circinans*, the organism responsible for the disease commonly known as onion smudge. It was stated by Walker (*J. Agric. Research*, 1923, **24**, 1036) that the chief factor which imparted the resistant property to the pigmented onion scales was a substance, or group of substances, either closely associated or identical with the red and yellow pigments present. Protocatechuic acid, the toxic entity which has now been isolated, is not present in the white scales. Although protocatechuic acid is widely distributed in plants as a constituent of many aromatic compounds, its occurrence in the free state has been reported only in a few cases. Its isolation from pigmented onion scales represents the third instance in which the acid has been found associated with the flavonol quercetin. The isolation of quercetin from pigmented onion scales was reported by Perkin and Hummel (*J. Chem. Soc.*, 1896, **69**, 1295). Upon alkaline fusion the pigment quercetin breaks up into phloroglucinol, oxalic acid and protocatechuic acid. The toxic action of the pure protocatechuic acid isolated, in dilutions of 1 part to 3000 parts of water, is identical with the toxic activity of the crude active aqueous extract from which it can be isolated. The toxicity of the crude aqueous extracts is, however, greater than the toxic effects that could be ascribed to the amount of protocatechuic acid isolated from a given unit of toxic extract. From the aqueous extract of 100 grms. of the dry pigmented scales approximately 0.1 grm. of the pure acid was isolated. It appears, therefore, that the quantity of protocatechuic acid isolated either represents only a fraction of the total present or suggests the alternate contingency that there are present still other phenolic substances or groups of substances to which some of the toxicity of the aqueous extract can be ascribed. A quercetin-free extract was still toxic to the fungus *Colletotrichum circinans*.

P. H. P.

Fluorescence of Honey in Ultra-Violet Light. **G. Orbán and J. Stitz.**

(*Z. Unters. Lebensm.*, 1928, **56**, 467-471.)—The 28 samples of honey examined in ultra-violet light (3,000 to 4,000 Å.) all showed luminescence, the intensity of which was dependent on the ultra-violet absorption, the colour and the thickness of the layer of honey used, and was unchanged when the honey was heated to 100° C., and then cooled to 30° C. Removal of water by evaporation produced an increase

in luminosity proportional to the increase in viscosity, and weakly caramelised honey showed a luminescence which was stronger for thin layers, but weaker for thick layers, than that of the unchanged sample. The method is of little value for distinguishing real and artificial honey, but the relation of the absorption to the powers of luminescence may sometimes serve as a guide to the origin of the sample (*cf.* Popp, *ANALYST*, 1926, 51, 540).
J. G.

Quantitative Determination of Oxymethylfurfural in Honey and Artificial Honey. J. Fiehe and W. Kordatzki. (*Z. Unters. Lebensm.*, 1928, 56, 490–492.)—Fiehe's criticism of Troje's method (*ANALYST*, 1929, 108) is justified by comparative experiments on genuine and artificial honeys by means of (1) Troje's method of titration with an alkaline solution of iodine; (2) quantitative precipitation by phloroglucinol; (3) Lenk's method (*Z. angew. Chem.*, 1917, 30, 49). Methods (2) and (3), only, gave reliable results, a heavy precipitate and marked reduction of the dilute alkaline copper solution being obtained, respectively, with artificial, but not with genuine honey. A solution of 100 grms. of sample was precipitated with zinc acetate and potassium ferrocyanide, and the filtered liquid extracted with ether thrice in 12 hours. The ethereal extract was well shaken with anhydrous sodium sulphate and an equal volume of petroleum spirit, and after 24 hours filtered and evaporated at a low temperature. The residue was then extracted with 20 c.c. of water, and 5 c.c. of the filtered extract used for each determination.
J. G.

Composition of Californian Walnut Oil. G. S. Jamieson and R. S. McKinney. (*Oil and Fat Ind.*, 1929, 6, 21–23.)—The chemical and physical characteristics of a sample of walnut oil, expressed in California, were found to conform to those generally accepted for European oils, with the exception of the iodine value, which was 161·7 (Wijs) and 158·5 (Hanus), whereas the usually accepted limits are 138 and 148 (Wijs). The oil contained 89·7 per cent. of unsaturated and 5·3 per cent. of saturated acids, and the composition is given as: Oleic acid, 17·6; linolic acid, 72·8; linolenic acid, 3·2; myristic acid, trace; palmitic acid, 4·6; stearic acid, 0·9; arachidic acid, trace; and unsaponifiable matter, 0·5 per cent. It should be noted that only a trace of myristic acid was found. The tables show: (1) The chemical and physical characteristics of the oil, (2) the fractional distillation of the methyl esters of the saturated acids; (3) analyses of the fractions from distillation of the methyl esters, and (4) figures for the saturated acids.
D. G. H.

Reactions of Soya Bean Oil. A. Richard. (*Ann. Falsif.*, 1929, 21 (240), 579–582.)—The presence of soya bean oil may be detected in olive or arachis oils by adding 10 c.c. of the sample to 1 c.c. of nitric acid and comparing the result with those produced on adding the same amount of acid to 10 c.c. of each of the pure oils. With arachis and olive oils more or less complete solidification occurs, increasing with time, and being practically complete in 24 hours. Soya oil remains liquid and also assumes a reddish brown colour which is absent with the

other oils. The coloration deepens in proportion with the percentage of soya oil, and 10 per cent. of soya bean oil may thus be detected in arachis or olive oils.

D. G. H.

Detection of Coconut Oil and Palm Kernel Oil by means of a Test for Lauric Acid. J. Grossfeld and A. Miermeister. (*Z. Unters. Lebensm.*, 1928, **56**, 423-437.)—The test for lauric acid previously described (*ANALYST*, 1929, 108) is modified as follows:—The fat (100 mgrms.) is saponified with 2.5 c.c. of 0.5 *N* alcoholic potassium hydroxide solution, the alcohol removed by evaporation, and an aqueous solution of the residue heated for 5 minutes on the water-bath in the presence of 2 c.c. of a 30 per cent. aqueous solution of glycerin, and precipitated with 2 c.c. of magnesium sulphate solution (150 grms. per litre). The liquid is filtered clear while hot, and in the presence of 10 per cent. or more of lauric acid (*i.e.* 20 per cent. of coconut oil) white flocks of precipitate form overnight. In negative or doubtful cases 1 grm. of oil is saponified with 0.4 c.c. of an aqueous 50 per cent. solution of potassium hydroxide and 2 c.c. of glycerin, 200 c.c. of water and 50 c.c. of the glycerin solution added, and the boiling mixture precipitated with 10 c.c. of reagent and filtered as before. A white opalescence is produced by 2.5 per cent. of lauric acid. Finally, to detect 0.5 per cent. of acid, the filtrate is shaken with 5 c.c. of dilute hydrochloric acid and 60 c.c. of ether, and the fatty acids removed and dissolved in 2.5 c.c. of 0.5 *N* alcoholic potassium hydroxide solution. The alcohol is removed, the residue dissolved in 2 c.c. of water, and the usual procedure followed. The method is not quantitative, but gave positive results in the presence of 0.3 mgrm. of coconut oil, and is unaffected by the presence of myristic, 4 mgrms. of capric, or 30 mgrms. of nonylic acid. By fractional steam distillation and fractional crystallisation of the magnesium salt from 1 grm. of oil it was possible to detect 10 and 1 per cent. of oil, respectively, and Don's distillation method (*Z. Unters. Lebensm.*, 1908, **16**, 705) is criticised on the ground that for small concentrations of lauric or myristic acids these acids are not completely removed. Dilution, or the addition of ammonium salts or methyl alcohol assists the separation of the magnesium laurate, but glycerin is preferable. The method was also applied to palm kernel, babassu, cotton-seed and ground nut oils (including the hardened oils) and to butter fat. Two rancid cotton-seed oils and one rancid oleostearin were found to be free from lauric acid, whilst hardened arachis and cotton-seed oils were found to contain it, and a sample of the former oil free from lauric acid gave a faint positive reaction after oxidation with potassium permanganate.

J. G.

Component Glycerides of Cacao Butter. C. H. Lea. (*J. Soc. Chem. Ind.*, 1929, **48**, 41-46T.)—The molecular proportions of the component acids of cacao butter are not widely variable, and this fact, coupled with the phenomenon of even distribution of fatty acids amongst the glycerides of a seed fat, is probably the cause of the fat possessing its peculiarly useful technical qualities. Further, the greater part of the mono-oleo-glycerides consists of oleo-palmito-stearin, and this class of glyceride is probably mainly responsible for the characteristic texture

and related properties of the fat. Oxidation of the fat by potassium permanganate in acetone shows the presence of only 2.5 per cent. of fully saturated glycerides, probably mixed palmito-stearic compounds. The content of mono-oleo-di-saturated glycerides lies between 73 and 85 per cent., and that of dioleo-mono-saturated glycerides cannot exceed 24.5, or that of triolein 12.5 per cent. The molecular ratio of saturated acids linked with unsaturated in the mixed glycerides is 1.4:1, the same as in coconut and palm kernel oils, and these results are supported by a study of the mono-azelaoglycerides in the oxidation products. Probably dioleostearin is present, and in greater amounts than dioleopalmitin in the dioleo-glycerides. The amount of triolein can hardly exceed 4 per cent. The following general estimate of the composition of cacao butter is suggested: Fully-saturated glycerides (mixed palmito-stearins), 2.5; mono-oleo-disaturated glycerides, 77; dioleo-mono-saturated glycerides, 16; triolein, 4 per cent.

D. G. H.

Component Glycerides of a Mutton Tallow. G. Collin, T. P. Hilditch and C. H. Lea. (*J. Soc. Chem. Ind.*, 1929, 48, 46-50T.)—The mixed fatty acids of the original tallow consisted of myristic 4.6; palmitic, 24.6; stearic, 30.5; oleic, 36.0; and linolic, 4.3 per cent. Complete oxidation was carried out by means of potassium permanganate in acetone; and 26 per cent. of fully saturated glycerides were found, of which the mixed fatty acids comprised: Myristic, 6.1; palmitic, 50.2, and stearic acid, 43.7 per cent., so that palmitic acid tends to accumulate in the fully saturated glycerides and stearic acid more in the mixed saturated-unsaturated part of the fat. Fractional crystallisation of the fully saturated glycerides indicated the presence of tristearin, palmitodistearin and dipalmitostearin, but individual glycerides were not isolated in the pure condition. The mixed saturated-unsaturated glycerides were found to contain 0.9 equivalent of saturated fatty acids per equivalent of unsaturated acids, and this was arrived at (i) from the percentage of fully saturated glycerides, the mean equivalents of the latter and of the original tallow, and (ii) from the composition of the fatty acids present in the mixed saturated-unsaturated glycerides (determined by difference between that of the fully-saturated glycerides and that of the whole fat). The limiting values for the classes of glycerides present are then: Fully saturated (chiefly mixed glycerides), 26; mono-unsaturated-di-saturated, 30-52; di-unsaturated-mono-unsaturated, 44-0; and tri-unsaturated, 0-22 per cent. Examination of the acidic products of oxidation suggests that the amount of mono-unsaturated glycerides tends towards the lower figure, *i.e.* there is probably a fairly large amount of di-unsaturated glycerides and a correspondingly small percentage of triolein.

D. G. H.

Colour Reaction of Diphenylamine. L. Desvergnès. (*Ann. Chim. anal.*, 1929, 11, 1-4.)—A solution of diphenylamine in alcohol gives the best results in producing a violet colour on addition of chlorine water, and the limit of sensibility is about 1 in 65,000. The presence of diethyldiphenylurea does not affect the colour. When testing for diphenylamine in "poudre B" it is best to extract with

ether, adding water to the filtered solution, to evaporate the ether slowly and, after cooling in ice, to add 10 c.c. of 95 per cent. ethyl alcohol, and to filter. It is necessary to add a sufficiency of chlorine water, as the violet coloration does not appear until the yellow colour has been destroyed. From 15 minutes to about 3 hours, according to the quantity of diphenylamine present, is required for the development of the colour.

D. G. H.

Analysis of Spirit of Nitre. L. Van Italie, A. J. Steenhauer and A. Harmsma. (*Pharm. Weekblad*, 1929, **66**, 15-22.)—Ten c.c. of the sample, 10 c.c. of 2 *N* potassium chlorate solution, and 5 c.c. of dilute sulphuric acid are shaken for 5 minutes in a stoppered flask, and diluted to 100 c.c. Ten c.c. of this are boiled with 3 c.c. of water and 2 c.c. of ammonia till 10 c.c. of liquid remain. To the cooled solution in a stoppered flask are added 1 gram. of potassium bromide and 15 c.c. of concentrated hydrochloric acid, and after 5 minutes, 10 c.c. of a 10 per cent. solution of potassium iodide. The mixture is titrated with a 0.1 *N* solution of sodium thiosulphate, and each c.c. of *N* potassium chlorate solution, reduced according to the equation $3\text{C}_2\text{H}_5\text{NO}_2 + \text{KClO}_3 = \text{KCl} + 3\text{C}_2\text{H}_5\text{NO}$, corresponds with 37.5 mgrms. of ethyl nitrite. The method gives satisfactory results when compared with the gasometric and other suggested methods.

J. G.

Determination of Chloral in Syrup of Chloral. Ch. Lormand. (*J. Pharm. Chim.*, 1929, **121**, 151-153.)—Chloral may be determined in its syrup by means of an ammoniacal and alkaline solution of silver nitrate, which is reduced by the syrup, with formation of silver, and silver chloride which remains in the ammoniacal solution. For 10 grms. of syrup containing 0.5 gram. of chloral, 50 c.c. of ammonia, 4 gram. of silver nitrate and 5 gram. of potassium hydroxide are used, and after 24 hours' contact the solution is heated to drive off excess of ammonia, slightly acidified with nitric acid, diluted to about 100 c.c. and again warmed, when the silver chloride dissolved in the concentrated salt solution is precipitated. After cooling, the silver chloride is filtered off, dried and weighed, and multiplied by 0.3844, to give chloral hydrate. A sample of syrup was found to give 4.76 per cent. of chloral by the alkalimetric, and 5.0 per cent. by the gravimetric method.

D. G. H.

Microchemical Reactions of Theobromine. M. Wagenaar. (*Pharm. Weekblad*, 1929, **66**, 1-5.)—Theobromine crystallises in rhombic, *d*-rotatory needles, m.pt. 329-330° C. (sublimes at 300° C.), refractive indices 1.51 (α) and 1.74 (β). It is soluble in cold water (1 in 1600), hot water (1 in 48), alcohol (1 in 1460), ether (1 in 17000), and in hot chloroform (1 in 105). Directions are given to obtain the best results with the following reagents, and the figures in brackets show limiting concentrations and smallest amounts detectable (in μ gram.), respectively, in each case:—Precipitation of theobromine (1:100 and 10), mercuric chloride (1:1000 and 5), gold chloride (1:100 and 10), silver nitrate (1:100 and 10), iodine in potassium iodide solution (1:1000 and 2), bromine in potassium bromide solution (1:1000 and 1), potassium bismuth iodide in the presence of a mineral acid (1:1000 and 2), and potassium antimony iodide (1:1000 and 1).

J. G.

Determination of Pilocarpine. P. Bourcet. (*Ann. Falsificat.*, 1929, 241, 23-24.)—Jaborandi leaves may contain a satisfactory proportion of total alkaloids and yet only very little pilocarpine. This may be determined as follows: 25 grms. of the leaves, ground to pass a No. 30 brass sieve, are moistened with 200 c.c. of 10 per cent. sodium carbonate solution and extracted with hot benzene in a Soxhlet extractor for three hours. The cooled benzene solution is shaken immediately with successive quantities of 30, 20, 20, and 10 c.c. of 1 per cent. sulphuric acid solution, the alkaloids passing into solution as sulphates. The green solution is filtered, neutralised to Congo red by means of ammonia, and oxidised with 1 per cent. potassium permanganate solution (a stronger solution may precipitate pilocarpine permanganate) until a drop of the permanganate solution gives a pink coloration persisting for a moment. The oxidised solution, rendered alkaline by addition of excess of ammonia, is extracted with twelve quantities of chloroform, the total chloroform solution (50 to 60 c.c.) being filtered, treated with fused and powdered sodium carbonate, and exactly neutralised by dropwise addition of 1:50 nitric acid solution. The neutral solution is evaporated to dryness in a small glass basin on a water-bath, and the cold residue is treated with a slight excess of acetone, which dissolves the impurities without dissolving an appreciable amount of the pilocarpine nitrate. This is collected on a Gooch crucible, dried below 100° C. and weighed. It forms a white, crystalline powder, and should melt at 174-175° C.; a melting point below 165° C. indicates unsuitability of the jaborandi for the preparation of pilocarpine.

It has been noticed, especially since the war, that certain samples of jaborandi show a satisfactory pilocarpine content if analysed as described above, whereas, if the benzene solution of the alkaloids is left for 24-48 hours, particularly in the light, less than one-half of the proportion of pilocarpine is obtained, and a slight deposit forms on the walls of the vessel. If, on the other hand, the powdered leaves are first extracted with a volatile solvent, such as benzene or petroleum spirit, and are treated with sodium carbonate and benzene only after this volatile solvent has been expelled, such retrogradation of the pilocarpine is not observed. No explanation is advanced for this behaviour.

T. H. P.

Biochemical.

Determination of Copper in Biological Materials. C. A. Elvehjem and C. W. Lindow. (*J. Biol. Chem.*, 1929, 81, 435-443.)—The wide distribution of copper in minute quantities in biological materials has been regarded, until lately, as accidental. The recent discovery by Hart, Steenbock, Waddell and Elvehjem (*J. Biol. Chem.*, 1928, 77, 797) of the importance of copper as a supplement to iron for haemoglobin building in the rat has shown the necessity for an intensive study of the distribution of copper in nature, and for a suitable method for the quantitative determination of this element. All the known methods were considered, and an accurate and rapid method has been outlined for the determination of copper in biological material which is a modification of the colorimetric method of Biazzo (*Ann. chim. appl.*, 1926, 16, 2), which was found to be the

most satisfactory. It is based on the fact that the neutral solution of a copper salt, when treated with a few drops of concentrated potassium thiocyanate solution and a few drops of pyridine, gives a green precipitate of the composition $\text{Cu}(\text{C}_6\text{H}_5\text{N})_2(\text{CNS})_2$, which is soluble in chloroform, and this is quantitatively removed by the chloroform from the solution in which it was formed. The green colour of the chloroform layer varies in intensity according to its copper content. This method is rapid, simple and accurate, and requires only a small weight of sample. Samples which contain 0.02 mgrm. of copper can be analysed with a high degree of accuracy. Care must be observed to prevent the introduction of any copper from the use of new porcelain dishes. A method is given for the removal of copper from the glaze of a porcelain dish, since one 3-inch evaporating dish may contain as much as 0.033 mgrm. of copper. The results of the Biazzo method are shown to agree closely with those from the xanthate method. Procedures are given for the analysis of substances rich in iron, for iron salts, and for milk and bones. Of ten samples of iron salts, only 2 were found to be copper-free. These figures point to the possibility of copper playing a rôle in many cases when beneficial effects of iron salts in the treatment of anaemia have been noted.

P. H. P.

Note on the New Ferricyanide Method for Blood Sugar. O. Folin. (*J. Biol. Chem.*, 1929, **81**, 231-236.)—Many workers have experienced difficulties with the new colorimetric ferricyanide method for the determination of blood sugar devised by Folin (*J. Biol. Chem.*, 1928, **77**, 421; *ANALYST*, 1928, **53**, 392-393), and, as little was said in the original paper about the keeping quality of the different reagents used in the method, such information as has since been obtained on these points is now given. One investigator stated that the dilute tungstic acid solution used for the protein precipitation must be fresh in order to give the low sugar values reported by Folin. Research has shown that the determining factors in that case were sunlight and toluene. Tungstic acid solutions kept in a dark cupboard without toluene gave perfectly water-clear extracts, and correct blood sugar values for at least 5 months, but in sunlight, with toluene added to preserve them, they deteriorated, and in a week gave 15 to 18 per cent. higher sugar values. Toluene in the presence of tungstic acid is decomposed by light, partly into reducing products, and partly into products which are oxidised in the presence of some other easily oxidisable substance (glucose). In the absence of tungstic acid toluene is not similarly decomposed. This destructive effect of light in the presence of tungstic acid may not be specific for toluene. Therefore the dilute tungstic acid solution need not be freshly prepared, provided that no preservative is used and that the reagent is not exposed to too much light. The sodium cyanide and carbonate solution keeps satisfactorily for several months, and so does the potassium ferricyanide solution if completely protected from light (in a brown glass bottle in a dark cupboard). The ferric iron solution has given most trouble. The author now uses gum ghatti in place of gum arabic, for it does not hydrolyse so easily, and is at least 5 times as effective as gum arabic as a protective colloid for Prussian blue. The preparation of this reagent is described in

detail. Oxidation with potassium permanganate is now included, even when gum arabic is used. The acid iron phosphate solutions containing gum ghatti have shown no signs of deterioration at the end of 2 months. The Prussian blue, by which the sugar reduction is measured, will remain in a clear uniform dispersion practically indefinitely, but the colour comparison must be finished promptly, as originally directed. P. H. P.

Determination of the Digestibility of Protein by Bergeim's Method.

W. D. Gallup. (*J. Biol. Chem.*, 1929, **81**, 321-324.)—The method of Bergeim (*J. Biol. Chem.*, 1926, **70**, 29) for the determination of the digestibility of food consists in "the addition to the food of small amounts of iron oxide (or other suitable substance)," followed by determination of the ratio of the amount of iron to the amount of any food substance in the diet and in the faeces, and calculation from this of the percentage of utilisation. Results by this method closely agree with those obtained by the usual procedure, *i.e.* measurement of the intake and output of nitrogen over a given period. The method, however, was found unsuitable for some diets which contain as much as 1 per cent. of soluble iron salts, and silica, which may be regarded as an insoluble compound and one that can be excreted with practical completeness in the faeces, has been used in place of iron oxide. A table shows a comparison of the results of the silica method, the iron oxide method and the usual method, when applied to the determination of the digestibility of the protein in a diet made up of natural foods. Albino rats were used for the study. The silica determinations gave results even more closely in agreement with those obtained by the usual method, than the iron determinations. Therefore, in carrying out digestibility studies by Bergeim's method with certain diets or under conditions which do not permit the use of iron oxide, silica in sufficient quantities can be used as a suitable substitute. When such a substitution is made, certain alterations in the procedure become necessary, but the method still retains most of its desirable features. P. H. P.

Micro Method for the Determination of Total Creatinine in Muscle.

S. Ochoa and J. G. Valdecasas. (*J. Biol. Chem.*, 1929, **81**, 351-357.)—A method is given for the determination of total creatinine in as small amounts of muscle as 5 to 100 mgrms., which is a slightly modified version of the original technique described by the authors (*Bol. Soc. Españ. Biol.*, 1927, **13**, 17). The muscle creatine is extracted and converted into creatinine by hydrochloric acid in the autoclave, then the proteins are precipitated by picric acid, and the creatinine is colorimetrically determined in the filtrate by the Folin technique. For the method from 5 to 100 mgrms. (preferably 20 to 50 mgrms.) of muscle are removed promptly from living animals under anaesthesia, and dropped into previously weighed Erlenmeyer flasks of about 50 c.c. capacity, which are kept tightly closed until they have been weighed again. A torsion balance, accurate to 0.1 mgrm., should be used, and the muscle samples should not be too much impregnated with blood. The weighed muscle is treated with 0.2 c.c. of 0.2 *N* hydrochloric acid for each mgrm. in weight (introduced by means of a standardised pipette graduated

in 0.01 c.c.), and the flasks are covered with tin-foil and heated in the autoclave to 120° C. for 25 minutes, cooled, 0.2 c.c. of pure 1.2 per cent. picric acid added for each mgrm. of muscle, and the contents then mixed and allowed to stand for 5 minutes. The abundant protein precipitate is separated by filtration. A fixed volume of fluid is pipetted from the clear filtrate, transferred to a flask, 0.5 volume of 5 per cent. sodium hydroxide solution is added, and the contents mixed. After standing for 5 to 8 minutes the colour comparison is made against a standard prepared as follows:—To 5 c.c. of a 0.002 per cent. creatinine solution in 0.2 *N* hydrochloric acid, 5 c.c. of pure 1.2 per cent. picric acid, and 5 c.c. of 5 per cent. sodium hydroxide solution are added, mixed, and left for 5 to 8 minutes when the standard is ready for use. The height of the standard (10 or 20 mm.), divided by the reading of the unknown and multiplied by 400, gives the total creatinine in mgrms. per 100 grms. of muscle. The mean error, as experimentally determined, can be given as 0.5 to 2 per cent. when all the operations are carried out with accuracy.

P. H. P.

Antineuritic Vitamin. II. Properties of the "Curative" Substance.

J. L. Rosedale and C. J. Oliveiro. (*Biochem. J.*, 1928, **22**, 1362–1367.)—During the preparation of extracts of the water-soluble vitamin from rice polishings it was noticed that, unless precautions were taken, alcoholic fermentation readily occurred at laboratory temperature, due to the presence of yeasts. Experiments on pigeons have been carried out to determine whether fermentation has any deleterious effect upon the extracts; results show that the antineuritic vitamin of an extract of rice polishings is destroyed by fermentation, and by sterilisation by filtration and by heat. The distribution of enzymes in the alimentary canal of the normal pigeon has been investigated, and the study extended to human cases. The potent curative extract of rice polishings contains sucroclastic and lipoclastic enzymes, but it has not been possible to show the presence of proteoclastic enzymes. Results indicate that during polyneuritis, metabolic disturbances occur which involve a certain amount of inactivation of the pancreas. In cases of "dry" beriberi, the pancreas has been found incapable of lipoclastic and tryptic digestion, but no deterioration of sucroclastic enzymes has been shown. The authors cannot conclude with Kon and Drummond (*Biochem. J.*, 1927, **21**, 632) that vitamin *B* bears relationship only to protein metabolism. Plimmer, Rosedale and Raymond (*Biochem. J.*, 1927, **21**, 913) found that the balance between vitamin *B* and protein was more difficult to demonstrate than that between carbohydrate or fat and vitamin *B*, but the experiments of Reader and Drummond (*Biochem. J.*, 1926, **20**, 1256) leave no doubt that protein is similarly affected. It is considered from the general results that the curative substance has at least some control over the action of pancreatic enzymes.

P. H. P.

Biological Inertness of Irradiated Mycosterols other than Ergosterol.

O. Rosenheim and T. A. Webster. (*Biochem. J.*, 1928, **22**, 1426–1428.)—The authors have worked up the mother-liquors resulting from the recrystallisation of large amounts of ergosterol from ergot, and have isolated a mycosterol which has

been proved to be identical with one prepared from ergot supplied by Messrs. Burroughs, Wellcome & Co., and for which the name "fungisterol," given by Tanret (*Ann. Chim. Phys.*, 1908, **15**, 313), is retained. Biological and spectroscopic examination showed the presence of less than 5 per cent. of ergosterol still in the specimens. The physical constants of the two specimens agreed with each other, but not with those of fungisterol, as described by Tanret. Apparently the latter product was still a mixture of several sterols, of which two further constituents have been isolated in the laboratories of Messrs. Burroughs, Wellcome & Co. These sterols, as well as the specimens of fungisterol, were found by the authors to be biologically inactive after irradiation, except for a slight action definitely due to the contaminating ergosterol. The results lend further confirmation to the view expressed previously by Rosenheim and Webster (*Biochem. J.*, 1928, **22**, 762; *ANALYST*, 1928, **53**, 551), that ergosterol is the only substance which can be converted into vitamin *D* by irradiation. It is interesting to note that zymosterol, which occurs together with ergosterol in yeast, is evidently not identical with fungisterol.

P. H. P.

"Hypervitaminosis" and "Vitamin Balance." L. J. Harris and T. Moore. (*Biochem. J.*, 1928, **22**, 1461-1477.)—Many writers have assumed that vitamins have no injurious effect when consumed in abnormally large amounts, and that an increased or diminished consumption of one vitamin does not affect the body's requirements for the others. With regard to the water-soluble vitamins no evidence is as yet available to suggest that any ill-effects result from overdosing, but in the case of fat-soluble vitamins, instances of supposed hypervitaminosis have been recorded, and attempts have been made to show that the fat-soluble and water-soluble requirements of the animal are, to some extent, inter-related. A thorough survey of the subject is now in progress, but results so far obtained are recorded, which, in a general way, definitely confirm the idea of a harmful effect resulting from excessive intake of certain materials rich in fat-soluble vitamins. Results show that young rats lost weight rapidly and died when receiving synthetic diets containing 0.1 per cent. of an irradiated (but not non-irradiated, over-irradiated, or heated) ergosterol (*i.e.* about 100,000 times a minimal protective dose). There was loss of appetite, ill condition of coats, etc., diarrhoea and inanition. No appreciable alleviation of these symptoms resulted when the vitamin *B* (marmite) allowance was increased to only 4 times the normally adequate level; in 2 cases where still further vitamin *B* (and *C*) (wheat-germ extract plus orange juice) was given, loss of weight was prevented. Results due to "toxicity" are contrasted with those due to mere loss of appetite. Apparently the rat is able to discriminate in its choice of diets; in a quantitative study rats refused food overloaded with irradiated ergosterol (5 per cent.). They showed lower growth rates compared with litter mates, and had rough coats, when cod-liver oil was substituted for 15 per cent. of arachis oil (inactive) in a ration which contained restricted allowances of vitamin *B* complex. Normal gestation always failed in rats receiving a diet containing 15 per cent. of cod-liver oil. Rats receiving

excessive doses of vitamins *A* and *D* concentrate from cod-liver oil, in conjunction with a diet deficient in the vitamin *B* complex, developed loss of hair and severe skin lesions. A close parallelism is suggested between the development of anti-rachitic and of toxic properties. It is obvious that any possibility of simple arithmetical equivalence in balance between vitamin *D* and the *B* vitamins is out of the question, yet, whereas the conception of a strictly quantitative balance cannot be tenable in any general sense, the possibility of a large excess of one vitamin emphasising the effects of deficiency of another cannot, as yet, be ruled out. Toxic effects at such enormous dosages should not in any way discourage the rational use of the properly standardised materials at the ascertainable correct physiological levels.

P. H. P.

Fluorescence of Some Vitamin *A*-containing Fats. R. S. Morgan and K. MacLennan. (*Biochem. J.*, 1928, 22, 1514-1522.)—A method has been devised by which the actual brightness of the fluorescence of a solid fat, illuminated by ultra-violet light filtered practically free from visible light, may be determined, and the colour expressed in terms of three additive primaries: red, green and blue. The apparatus for the measurement of fluorescence is described in detail, and diagrams are given. Actual colour readings are measured when a standard lamp giving white light replaces the filtered ultra-violet light. The unsaponifiable matter from cod-liver oil contains a brightly fluorescent substance. Curves and tables show the effect of the addition of unsaponifiable matter from cod-liver oil on the fluorescence of two fats, one already slightly fluorescent (*jus*), and the other brightly fluorescent (hardened coconut oil). Although there is a close association between vitamin *A* and a characteristic fluorescence, yet discrepancies occur. No fat containing vitamin *A* has yet been observed that does not also show the fluorescence associated with it, and an explanation of the discrepancies may be that, whereas vitamin *A* is actually a brightly fluorescent substance, in certain circumstances other substances may be formed in oils, giving a fluorescence somewhat similar to that due to the vitamin. No connection seems to be apparent between fluorescence and vitamin *D*. The fluorescence of butter or butter fat is yellow in colour, but the normal fluorescence of margarine is blue. This difference cannot be accounted for solely by the known differences in vitamin content. The blue fluorescence of margarine can be modified as follows: (*a*) By variation of the fat mixture; certain vegetable fats fluoresce bright blue, whilst the fluorescence of oleo and *jus* is pale greenish; (*b*) by the addition of unsaponifiable matter from cod-liver oil; the first small additions markedly increase the brightness and diminish the blueness of the fluorescence; (*c*) by variation of the nature of the pigment present; some pigments depress the fluorescence more markedly than others. The following table shows that samples that respectively match Danish butter-fat and New Zealand or Irish butter-fat in the quality of their fluorescence, also match them in the actual colour by ordinary illumination. Here, as would be expected, the greater opacity of the *jus* increases the brightness by reflected light.

The actual colour by reflected light of samples matching in fluorescence was as follows:—

	Shade.	Quality.		
		Red.	Green.	Blue.
Danish butter fat I	58	47	40	13
Oleo+0.8 per cent. red palm oil+unsap. to vitamin potency of butter fat ..	57	48	41	11
Jus+0.8 per cent. red palm oil+unsap. ..	69	47	39	14
New Zealand butter-fat	45	51	40	9
Jus+1.6 per cent. red palm oil+unsap. ..	53	52	39	9

A sample of oleo coloured with sufficient red palm oil to match it with butter-fat, and with sufficient unsaponifiable matter from cod-liver oil to bring it up to butter-fat in vitamin A potency, exactly matches butter-fat in fluorescence. P. H. P.

Bacteriological.

Quantitative Determination of Indole in Bacterial Cultures. H. B. Pierce and R. B. Kilborn. (*J. Biol. Chem.*, 1929, 81, 381-387.)—The method of Bergeim (*J. Biol. Chem.*, 1917, 32, 17) for the determination of faecal indole has been adapted to the quantitative determination of indole in bacterial cultures. Bergeim's method consists in a steam distillation of a faeces suspension in an alkaline medium to remove phenols. The distillate, which contains indole and ammonia, is redistilled from an acid solution or treated with permittit to remove ammonia. A portion of the ammonia-free distillate is treated with β -naphthoquinone sodium monosulphonate, and the blue indole compound thus formed is extracted with chloroform, and determined colorimetrically. For the bacterial cultures the distillation was carried out at a P_H of 8.5 to 10.0, and permittit proved to be entirely satisfactory for the removal of ammonia from the distillate. Steam should be passed through the contents of the distilling flask during the entire period of distillation, and the solution remaining in the flask at the end of the period should be approximately 150 c.c. An average of 91 per cent. of the indole added to peptone water or to bacterial cultures in peptone water has been recovered by use of this method. The average percentage of indole recovered from aqueous solutions ranged between 94 and 97. Fellers and Clough (*J. Bact.*, 1925, 10, 105) and Zoller (*J. Biol. Chem.*, 1920, 41, 25; *ANALYST*, 1920, 45, 177) have criticised Bergeim's method on the grounds that the procedure is involved, and the reagent very difficult to obtain. This method for bacterial cultures is not quite quantitative, but it is more nearly so than that of Fellers and Clough, and once the technique is standardised, the procedure is not involved. The reagents required are comparatively inexpensive. If the solution containing this reagent (a 2 per cent. solution) is kept in an ice box, it does not deteriorate during a period of 3 days. When a precipitate forms the reagent should be discarded. P. H. P.

Toxicological and Forensic.

Distribution of Bismuth in the Organs after Injection of Aqueous Solutions. R. Fabre and M. Picon. (*J. Pharm. Chim.*, 1929, 121, 97-112.)—Aqueous solutions of ammoniacal bismuth citrate and bismuth cacodylate were used for injecting into rabbits. In the former case the kidneys were particularly affected, and the hair helped to excrete the bismuth, probably supplementing the insufficiency of the renal separation. With the cacodylate the toxicity was much less, and the liver retained more bismuth than the kidneys. It is concluded generally that the cacodylate and campho-carbonates of bismuth are less toxic than the ammoniacal citrate, and tables are given showing the proportions of bismuth found in the various organs after injection. D. G. H.

Organic Analysis.

Application of the Hydrogen Value to Unsaturated Fatty Acids. H. J. Waterman, S. H. Bertram and H. A. Van Westen. (*J. Soc. Chem., Ind.*, 1929, 48, 50-51T.)—The hydrogen value (*ANALYST*, 1929, 54, 119) has now been determined for elaidic, linolic and stearolic acids, and in each case pure stearic acid was the product of hydrogenation. The results with elaidic acid are considered as standard measurements. The results of the hydrogenation of $\Delta^9:12$ -linolic acid showed that two double linkings are saturated (not 1 double and one triple), 2 molecules of hydrogen being consumed per molecule of linolic acid. Stearolic acid behaved towards the thiocyanogen solution as though almost completely saturated, and towards iodine solution in accordance with one double linking, whereas treatment with hydrogen with palladium catalyst proved the presence of a triple linking. D. G. H.

Conversion of Higher Fatty Acids into their Barium Salts. H. H. Escher. (*Helv. Chim. Acta*, 1929, 12, 103-105.)—Owing to the readiness with which both the acids and their barium salts separate and include one another, quantitative conversion of the higher fatty acids into their barium soaps by means of barium salts or aqueous barium hydroxide is difficult. The titration of solutions of fatty acids in concentrated or dilute alcohol or in methanol with aqueous 0.1 *N* barium hydroxide solution gives low results, which are improved but not rendered quite satisfactory by adding a large excess of alcohol, by heating, and by adding the baryta very slowly and with vigorous swirling of the liquid.

Conversion of the fatty acids into their barium salts proceeds quantitatively and more easily if a methanol solution of barium hydroxide is used. In this way solutions of stearic, palmitic and oleic acids, and also those of oleic acid dibromide and linolic acid tetrabromide in methanol, ethanol, ether, chloroform, carbon tetrachloride, dichloroethane, etc., may be titrated sharply. Crystallised baryta (+8H₂O) dissolves to the extent of about 30 per cent. in commercial pure methanol and, although the latter contains about 0.1 per cent. of acetone, the solutions

maintain their titre and keep clear and colourless for a year. The solution is kept in a vessel closed by a soda-lime U-tube, 40 cm. long, drawn out at the end to 1 mm.; the rubber of the syphon tubes does not swell and is only slightly attacked. The "sticking" of the glass-rod cock when only occasionally used may be obviated by frequent loosening or by using rubber tubing which has been artificially aged in a hot solution of barium hydroxide and methanol.

T. H. P.

Preparation of Styrolenes. Detection and Identification of β -Phenylethyl Alcohol. S. Sabetay. (*Bull. Soc. Chim.*, 1929, (iv), 45, 69-75.)—Distillation of β -phenylethyl alcohol over anhydrous potassium hydroxide furnishes an almost quantitative yield of styrolene, other analogous alcohols behaving similarly. The reaction is characteristic of the group $\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, and is explainable by the facility with which a double linking is formed adjacent to the benzene nucleus owing to the influence of the phenyl radical on the mobility of the neighbouring hydrogen atom.

The identification of β -phenylethyl alcohol by means of such crystalline derivatives as its phenylurethane, diphenylurethane, acid phthalate, monobenzylphthalate, etc., is difficult in presence of geraniol, rhodinol, phenylpropyl alcohol, etc., and such mixtures are not easily resolved by simple distillation. In these cases, it is necessary only to distil the mixed alcohols over anhydrous potassium hydroxide, to collect the first few c.c. of distillate, and to test this for styrolene by its odour and by means of the dibromide, which crystallises readily from 80 per cent. alcohol and melts at 72°C . Although rhodinol, geraniol, etc., also form brominated derivatives, these are not solid under the conditions employed. The minimum amount of the dibromide detectable in this way varies, but the quantity formed gives an approximate indication of the quantity of β -phenylethyl alcohol present.

T. H. P.

Quantitative Separation of Dextrins and Gum Arabic. A. Hamy. (*Ann. Falsificat.*, 1929, 241, 24-26.)—The methods used for the determination of gum arabic, such as precipitation by alcohol or the formation of gum-iron compound, give erroneous results in presence of highly condensed dextrins, owing to simultaneous precipitation of these. The method now suggested for use in such cases depends on the fact that treatment of an aqueous gum solution with basic lead acetate yields an abundant precipitate which, in presence of a sufficient quantity of glucose or sucrose, dissolves completely; this solvent action may, however, be annulled by addition of alcohol. The procedure is as follows: Twenty c.c. of the syrup of half-concentration and 23 c.c. of 95 per cent. alcohol are made up to volume with water in a 55 c.c. flask, and the liquid left for some hours to deposit the dextrins and then filtered through a close filter-paper into a 50 c.c. flask. The 50 c.c. of filtrate are treated with 90 c.c. of water containing glucose and sucrose in such quantities that the final mixture contains 5 and 8 grms., respectively, of these sugars, and then with 42 c.c. of 95 per cent. alcohol and 15 c.c. of basic lead acetate. After being shaken three or four times, the liquid is left until the next morning, when the supernatant liquid is either siphoned off

or, if there is gum in suspension, decanted on to a Gooch crucible. The deposit is centrifuged in two 45 c.c. tubes, vessel and precipitate being washed with 50 c.c. of 5 per cent. basic lead acetate solution to remove excess of dextrans and alcohol. After centrifuging, the precipitate in each tube is mixed with 4.3 c.c. of a 75 per cent. sugar solution, which dissolves it partially, and is then mixed well with 35 c.c. of a mixture of 120 c.c. of 95 per cent. alcohol, 27 c.c. of basic lead acetate solution, and 160 c.c. of water. The covered tubes are left to deposit and afterwards centrifuged, the precipitate being dissolved in 4 per cent. acetic acid (turbidity of the solution is of no account) and the gum precipitated by about 10 times the volume of alcohol. On the following day the precipitate is collected on a Gooch crucible, dried at 110° C., weighed, calcined and weighed again. The difference in weight represents the anhydrous gum contained in the 50 c.c. of filtrate taken. Trial determinations gave good results.

T. H. P.

Study of the Digitonin Ergosterol Complex. M. H. Pénau and Z. Hardy. (*J. Pharm. Chim.*, 1929, 121, 145–151.)—Digitonin forms a complex with ergosterol, which under certain conditions is practically insoluble. This complex may be resolved into its components again by prolonged treatment with boiling toluene. The conditions for determination of ergosterol by means of the complex are as follows. The ergosterol (175 mgrms.) is dissolved on a water-bath in 99 per cent. alcohol, cooled, made up to 100 c.c., and 10 c.c. put into a weighed centrifuge tube, 9 c.c. of the digitonin solution (1 per cent. by volume in 99 per cent. alcohol) added (measured at the same temperature, 15° C.), and 2 c.c. of water. After standing for 18 hours the mixture is centrifuged for 15 minutes, the supernatant liquid decanted, and the precipitate washed with 4 c.c. of Caminade's solution (water-alcohol-acetone), again centrifuged, the washing solution decanted, and the tube dried and weighed. One gram. of the complex contains 250 mgrms. of ergosterol.

D. G. H.

Universal Indicator which gives the Colours of the Spectrum over a P_H Range of 3 to 11.5. H. W. Van Urk. (*Pharm. Weekblad*, 1928, 65, 1246–1249.)—The indicator contains 0.1 gram. of methyl orange, 0.04 gram. of methyl red, 0.4 gram. of bromthymol blue, 0.32 gram. of naphtholphthalein, 0.5 gram. of phenolphthalein, and 1.6 grms. of cresolphthalein in 100 c.c. of 70 per cent. alcohol. One drop is added to 10 c.c. of the solution to be tested, and the colour changes from red-orange (P_H 3) to yellow-orange (P_H 5), yellow (P_H 6.5), green (P_H 8), green-blue (P_H 9), violet (P_H 11), and red-violet (P_H 12).

J. G.

Inorganic Analysis.

Reaction of Cupric Salts with Thiosulphate. J. Hanus and V. Hovorka. (*Trav. Chim. Czechoslovak*, 1929, 1, 65–82.)—Published investigations of this reaction show discordant results. The authors find that the precipitates deposited, when cupric salt solutions are boiled with a thiosulphate, consist of

mixtures of cuprous and cupric sulphides and free sulphur in proportions varying with the duration of the boiling, the amount of thiosulphate added, and the degree of acidity of the solution. Prolonged boiling results in a greater proportion of cupric than cuprous sulphide, and the percentage of the latter in the precipitates from neutral solutions reaches a maximum when the initial solution contains copper and thiosulphate in the molecular ratio 1:2.5-3. With a large excess of thiosulphate almost pure cupric sulphide mixed with sulphur is obtained. In acid solution decomposition of the thiosulphate itself alters the composition of the precipitates. The order of the operations also varies the result, since less cupric sulphide is formed when the whole amount of thiosulphate is added to the boiling acidified solution of cupric salt than when the cold mixture is subsequently heated to boiling.

For analysis, the precipitate was collected on a Gooch crucible with a filter-paper (Adams' filter for extracting fats), and washed with hot water, alcohol, and ether, the free sulphur being then extracted by means of nitrobenzene at 100° C. The residual precipitate was treated in a beaker with two successive quantities (15 to 25 c.c.) of 10-15 per cent. silver perchlorate solution, and the resulting mixture of silver sulphide and silver washed until free from silver ion, and afterwards treated twice or thrice with 40-50 c.c. of 6 per cent. ferric nitrate solution, which brings the metallic silver into solution but leaves the silver sulphide unchanged. The filtrate, acidified with nitric acid, was concentrated to 100-120 c.c., allowed to cool, and titrated with 0.1 N potassium thiocyanate solution. This gives the silver formed from the cuprous sulphide in accordance with the equation, $\text{Cu}_2\text{S} + 4\text{AgNO}_3 \longrightarrow 2\text{Cu}(\text{NO}_3)_2 + \text{Ag}_2\text{S} + 2\text{Ag}$ (cupric sulphide giving only silver sulphide), and hence the cuprous sulphide. The initial amount of cupric salt being known, the cupric sulphide was readily determined by calculation. When the copper was not totally precipitated, the residual amount in the first filtrate was determined electrolytically.

T. H. P.

Titration of Thallous Salts with Permanganate in Hydrochloric Acid Solution. A. Jílek and J. Lukas. (*Trav. Chim. Czechoslovak.*, 1929, 1, 83-94.)—The incompleteness of the oxidation of thallous to thallic salts by permanganate in presence of hydrochloric acid, and the consequent necessity of using an empirical factor in such determinations, may be obviated by the addition of an alkali chloride, which forms a double salt with the thallic chloride formed and thus suppresses hydrolysis. The solution to be titrated is treated with 2 grms. of potassium chloride, repeatedly evaporated with hydrochloric acid to remove other acids, diluted and twice treated with 2-5 c.c. of sulphurous acid solution, the excess of sulphur dioxide being expelled by boiling after each addition. After a further addition of 10 c.c. of concentrated hydrochloric acid, the liquid is made up to 150 c.c. and titrated with 0.02 N permanganate solution. The excess of permanganate required to produce the pink end-point is determined by a blank experiment, and the result corrected accordingly; 1 c.c. of 0.02 N permanganate corresponds with 0.0020439 gm. of thallium.

T. H. P.

Iodimetric Determination of Iron. E. C. Grey. (*J. Chem. Soc.*, 1929, 135, 35-39.)—The iodimetric method for the determination of iron, first proposed by Mohr (*Ann.*, 1858, 105, 53) yields trustworthy results under the following conditions: The ash of the sample is evaporated repeatedly with hydrochloric acid until any insoluble residue is colourless, then dissolved in water and the hydrochloric acid content of the solution adjusted so that there is not less than 0.4 c.c. of the concentrated acid in 10 c.c. (The volume of the acid used should be noted, for a control may be necessary to correct for the iron which it may contain.) If copper is present, the solution is treated with an excess of ammonia, the precipitate collected on a filter, washed, and re-dissolved in hydrochloric acid. To each 10 c.c. of the solution is then added 0.33 gm. of potassium iodide dissolved in 5 c.c. of water. The liberation of iodine is complete in three minutes at 15° C. The solution is next diluted, sodium acetate is added if desired, and the iodine is titrated with very dilute standardised thiosulphate solution. W. P. S.

Gravimetric Method for the Micro Determination of Molybdenum. J. B. Niederl and E. P. Silbert. (*J. Amer. Chem. Soc.*, 1929, 51, 376-377.)—From 3 to 5 mgrms. of the sample, which should not contain non-combustible or non-volatile substances other than molybdenum, are placed in a micro porcelain combustion boat, a drop of nitric acid is added, the boat is inserted in a combustion tube and heated gradually. When all fumes have disappeared the boat and its contents are heated for a further five minutes, cooled, and the molybdenum trioxide is weighed. The heating employed must not be excessive since molybdenum trioxide is volatile at temperatures above 450° C. W. P. S.

The Phosphoric Ion as a Sensitive Reagent. Differentiation of Antimony and Tin. T. G. Y. Arnal. (*Chim. et Industrie*, 1928, Oct.; *Ann. Chim. anal.*, 1929, 11, 11-12.)—On mixing sodium molybdate and antimony trichloride solution there is formed a yellowish precipitate soluble in excess of antimony trichloride, and the reagent thus produced is very sensitive to the phosphoric ion. If an ortho-phosphate is then added a blue coloration or precipitate results. If a solution of orthophosphate is added to stannous chloride followed by sodium molybdate, a blue coloration forms changing to rose. In the unknown solution tin is first sought with sodium molybdate, and to another portion an orthophosphate solution is added followed by sodium molybdate. If a blue coloration persists antimony is present. A table of reactions of the reagent is given. D. G. H.

Physical Methods, Apparatus, etc.

The Ultraviolet-Detector as an Aid in distinguishing Real Amber from its Imitations. G. Kostka. (*Chem. Ztg.*, 1929, 53, 117-118.)—When exposed to the light from a Hanau quartz lamp filtered so that only rays of λ 440 to 280 $\mu\mu$ pass, natural amber exhibits intense fluorescence which varies from yellowish-green or greenish to bluish-white. With pressed amber (ambroid), the

fluorescence is weaker and yellowish-green. The phenol-formaldehyde resins show no fluorescence, and the urea-formaldehyde resins, and the casein preparations, and the plastic cellulose derivatives pale bluish or bluish-white fluorescence.

T. H. P.

Reviews.

DIE MASSANALYSE. ZWEITER TEIL: DIE PRAXIS DER MASSANALYSE. (THE PRACTICE OF VOLUMETRIC ANALYSIS.) By I. M. KOLTHOFF, in collaboration with H. MENZEL. Pp. 512. Berlin: Julius Springer.

In spite of the large volume of Kolthoff's publications in recent years, in this book the high standard of his work is maintained. The author does not claim the work to be exhaustive, nor does he expect it to replace the standard works on volumetric analysis; he hopes rather that it will be complementary to them. The book contains a critical survey of a number of typical volumetric processes, most of which have been studied by the author. The "personal" nature of the book will be realised when it is stated that there are nearly 150 references to Kolthoff's published researches, as well as frequent mention of his unpublished work; a considerable number of references to other authors are, however, also given, and the whole subject appears to be treated in an impartial manner. The titles of the chapters are: Measuring Apparatus for Volumetric Analysis; Practical Foundations; Alkalimetry and Acidimetry; Neutralisation Reactions; "Depression" Reactions; Hydrolytic Precipitation and Complex-forming Reactions; Special Methods in Alkalimetry and Acidimetry; Titrations with Silver Nitrate (Argentimetry); Formation of Complexes (Mercurimetry); Indicators in Oxidation and Reduction Processes; Permanganate (Oxidimetry); Iodimetry; Practical Methods of Iodimetry; Titrations with Potassium Iodate; Titrations with Potassium Bromate; Titrations with Dichromate; Other Volumetric Reagents. There is an appendix containing atomic and equivalent weights useful in volumetric work, and also an author index and a very complete subject index.

There are two special features in this interesting book; one is the use of the "rational" atomic weights recommended by Schoorl (*Z. anal. Chem.*, 1918, 57, 209), which allow for the fact that weighings in analytical work are invariably made in air and not corrected for the buoyancy effect. The other is the special attention paid to the question of purifying and testing the standard materials, *e.g.* sodium thiosulphate, sodium carbonate, silver nitrate, and oxalic acid, from which volumetric solutions are frequently prepared by direct weighing. The work is quite up to date; it contains examples of the application of the adsorption indicators recently developed by Fajans, and of the use of 8-hydroxyquinoline as a precipitation reagent in the volumetric estimation of zinc, magnesium,

calcium, and aluminium (*cf.* Berg, *ibid.*, 1927, 71, 23 and 171; Hahn and Vieweg, *ibid.*, p. 122).

Although this is not a book for the beginner in volumetric analysis, yet an analyst with some experience will find it an invaluable guide, to be used alongside his standard practical works, in the choice of accurate methods. Part of the work has now been published as an English translation (*cf.* ANALYST, 1929, 194).

S. GLASSTONE.

ANALYTICAL CHEMISTRY. Vol. II. QUANTITATIVE. BASED ON THE TEXT OF F. P. TREADWELL. W. T. HALL. Seventh Edition. Pp. xiii+848. New York: John Wiley & Sons, Inc.; London: Chapman & Hall. 1928. Price 30s. net.

A novel feature of the seventh edition of Professor Hall's adaptation from Treadwell's text is an Appendix outlining a course of instruction at the Massachusetts Institute of Technology. This outline accounts almost entirely for the additional 40 pages and, unfortunately for the general reader, its appearance coincides with an increase of 5s. in the price of the book. A number of methods published since the appearance of the sixth edition (ANALYST, 1924, 49, 608) have been incorporated in the text, including Moser and Niessner's recent separation of aluminium from beryllium (ANALYST, 1928, 53, 401).

It need not be repeated here that the volume under review is one of the indispensable reference-books for the laboratory, and it will doubtless continue to occupy that enviable position owing to its wide circulation, which ensures frequent opportunities for revision. If that is well done—both by addition of new important matter and excision of all that is becoming obsolete—the author will have deserved the gratitude of the analytical fraternity.

It is in an endeavour to help towards more uniform reliability, not in a spirit of adverse criticism, that the writer has selected the following points for discussion, as he believes them to constitute minor flaws in an otherwise excellent piece of work.

The student confronted with a pyrosulphate fusion must imagine it a formidable undertaking. He is told that "this is a difficult fusion to make satisfactorily and requires time and patience" (p. 115), and that the attack of *precipitated* iron-aluminium oxide is "usually complete in 2-4 hours" (p. 110). Were this so, the researches of the reviewer and his co-workers on the earth acids and other refractory oxides—largely a spare-time pursuit which so far has necessitated several thousand bisulphate fusions—could never have been carried out. As a matter of fact, the fusion of an ignited oxide precipitate is a matter of only a few minutes, provided the oxide is in a state of fine subdivision; this is ensured by the incorporation of pulped filter fibre before or after precipitation. The addition of filter pulp not only imparts porosity to the ignited precipitate, but accelerates the filtration, washing, and ignition to constant weight; it is, in the writer's opinion,

one of the most valuable expedients ever introduced into analytical practice, and should be inculcated as part of general analytical technique.

The text-matter dealing with the determination of bismuth (p. 180-183) could, no doubt, be made to gain by a process of revision. As many as six methods are given: (1) Precipitation with ammonium carbonate and ignition to oxide; (2) determination as sulphide, involving extraction with carbon disulphide; (3) reduction to metal by cyanide fusion; (4) reduction by alkaline formaldehyde; (5) electrolysis; and (6) determination as phosphate. Of these methods, (2) to (4) are, to say the least, given undue prominence, as they are of doubtful practical value, whilst the useful oxychloride method—certainly superior to the three methods cited—is not mentioned at all. The directions for the method *par excellence* (determination as phosphate) are inadequately given in five lines, followed by this comment: "Sometimes, when the bismuth solution is not sufficiently dilute or too much free acid is present, the filtrate comes through turbid. In such cases, wash the filter with hot water and return the filtrate to the original beaker." All will agree that this is not quite good enough for "Treadwell"; "too much free acid" is almost synonymous with incomplete bismuth precipitation, and if the exact conditions for the operation were specified (*cf.* ANALYST, 1920, 45, 435), the possibility of such faulty work would be excluded.

For the determination of lead in ores containing barium sulphate (p. 178), the treatment prescribed is acid attack, followed by evaporation with sulphuric acid until fumes appear, dilution with water, and collection of the mixed sulphate precipitate, followed by the familiar ammonium acetate treatment; according to the text, the lead dissolves, whilst the barium sulphate remains insoluble. If, as is more usually the case, the baryta content of the ore is small and the lead content high, the results obtained by this method may go unchallenged; but its principle is faulty, for the sulphates re-precipitated by the dilution of the sulphuric acid contain more or less lead in an acetate-insoluble form, probably as mixed crystals of $(\text{Ba}, \text{Pb})\text{SO}_4$.

An important separation in the hydrogen sulphide group of metals is that of the sulpho-acids from the sulpho-bases by means of alkali sulphide. This separation of the two sub-groups from one another is neither easy nor always perfect; it may necessitate a repetition of the treatment according to the nature and relative proportions of the elements to be separated, whilst the presence or absence of mercury, tin, or cadmium has a very important bearing on the success of the operation. Yet the directions are condensed into a few lines (p. 219), not even the concentration of the reagent or the time of digestion being given. Considering that, on the other hand, the determination of, *e.g.* carbon dioxide occupies some 18 pages, it must be admitted that the treatment of the subject is not uniformly thorough.

The systematic weeding-out from the literature of antiquated methods is a cause which all scientific authors, especially those engaged in teaching, should have at heart. A widely-circulated book like the present might well contain an *Index*

Expurgatorius of methods that have been definitely proved to be untrustworthy. The separation of selenium from tellurium by cyanide fusion (p. 262) is one of the processes that have outlived their usefulness. The description of the procedure is followed by a note to the effect that it gives "slightly low results for tellurium and high values for selenium"; but, since the two elements can be separated more accurately by other methods, there seems to be no valid reason why this process should still be given. It is far better to err on the side of incompleteness while selecting only the very best from the mass of available material, than to retain methods that have been condemned by more than one investigator.

W. R. SCHOELLER.

ARTIFICIAL SILK. By Dr. FRANZ REINTHALER. Enlarged and Revised Edition. Translated from the German by F. M. ROWE, D.Sc. Pp. xii+276. London: Chapman & Hall, Ltd. 1928. Price 21s. net.

This book is not merely a translation of Dr. Reinthaler's well known monograph, but is a revised and enlarged English edition, in the preparation of which both author and translator have collaborated. The result is a most useful and practical book on Artificial Silk in every aspect of the subject, and we are indebted to Professor Rowe for making this work available to English readers. A considerable deal of new matter has been introduced, together with a large number of illustrations, so that the book is somewhat longer and more up-to-date than the original. It is now a very complete summary of the manufacture, properties and uses of all types of artificial silk, including the ether silk of Lilienfeld. The object has been to give some account, at least, of all phases of the subject, and in this the authors have been very successful. The viscose process, exceptionally, has been treated in much greater detail. The illustrations of machinery represent almost exclusively those of German manufacture, as it is felt that the corresponding British products are sufficiently illustrated in E. Wheeler's "The Manufacture of Artificial Silk, 1928." A number of British and foreign companies have co-operated by supplying information and specimens for illustration.

The treatment of each process is systematic, beginning with the raw material, preparation of the cellulose, dissolving, spinning, finishing, etc. The "viscose process" occupies 50 pp., "artificial silk from cellulose compounds," in which are included acetate silk and ether silks, 23 pp. Chapters follow on the properties of artificial silks, on testing and on dyeing artificial silks and staple fibre, with four final chapters dealing with applications and uses of artificial silks and the economic position of the industry. The chapters dealing with manufacture are especially well done, and they include a brief account of Dr. Lilienfeld's cold viscose process (Eng. Pat. 212865), by which artificial silk can be produced of a tenacity exceeding that of natural silk, the strength being greater than 5 grm. per denier. The Lilienfeld ether process is also given with some detail and, throughout, the properties of this silk are included among those of the other types.

The chapter on dyeing does not attempt to detail processes, but gives a very useful account of the different problems and difficulties that arise in dyeing, and indicates the most satisfactory methods to employ in order to avoid faults. The chapters other than those dealing with manufacture are a little more open to criticism for two reasons. In the first place the authors' desire is obviously to make the book available to the non-scientific reader, for which purpose matter is introduced which is often the reverse of explanatory: secondly, the translator often follows the German idiom so closely that the style becomes confused. Two examples of the former may be quoted—"Now that the action of acids and alkalis on cellulose has been considered, the behaviour of salts formed by the action of acids on metals, oxides and hydroxides, is of interest" (p. 10). And again—"The copper number represents the number of grms. of copper absorbed from Fehling's solution by 100 grms. of dry commercial cellulose" (p. 34). The use of the words "absorbed" and "commercial" is certainly misleading.

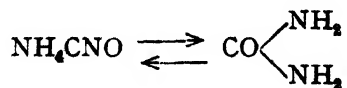
The book contains about 30 per cent. more matter than the German edition, but, speaking from memory, we should say that it is more than twice as thick and three times as heavy. In these days of many books and limited accommodation it is a great pity that so much unnecessary bulk and weight should be put into a volume of this sort. The paper employed is needlessly thick, and the case in which it is bound is far too light, a combination which will certainly not make for durability if the volume is much used. On taking down, at random, a book of the same thickness, Mellor's "Modern Inorganic Chemistry," it was found to contain three times as many pages and to be far more comfortable to handle.

These, however, are minor criticisms. The book is an admirable, up-to-date treatise, excellent both in its completeness and in the terseness with which each section is handled.

C. DORÉE.

MOLECULAR REARRANGEMENTS. By C. W. PORTER, Professor of Chemistry in the University of California. 167 pp. New York: The Chemical Catalog Company, Inc. 1928. Price 4 dollars.

Organic Chemistry has just celebrated its hundredth birthday. In 1828 Wöhler described the first synthesis of an organic compound from an inorganic source, and observed the first molecular rearrangement namely, that of ammonium cyanate into urea:



Since then it has been shown by Walker, in 1895, that the reaction is reversible, but the question how and why ammonium cyanate rearranges itself into urea is still unanswered. To Wöhler's molecular rearrangement numerous other cases have been added during the last hundred years, involving migration from carbon

to nitrogen, from nitrogen to carbon, from carbon to carbon, from oxygen to carbon, etc. Each individual case has been studied with care and skill involving the work of such masters of organic chemistry as Kolbe, Hantzsch, Meerwein, and others, but the mystery still remains unsolved; we have still no real explanation of the why and wherefore of these molecular rearrangements. A very suggestive generalisation which seemed to account for the mechanism of these reactions was put forward by Robinson in 1920, but Professor Porter dismisses it as being unacceptable, since it involves "the formation of intermediates that cannot be isolated" (p. 96).

Professor Porter reviews the main phenomena of molecular rearrangements in the first five chapters, and then deals in the remaining two chapters with the problems of mutarotation, racemisation, and that greatest of all mysteries the Walden inversion. The facts are clearly mustered, and the material presented in a very attractive way. Professor Porter is to be congratulated on the lucid manner in which he has dealt with his subject matter. It is noteworthy that he has not included Fischer's acyl migration in a book which will certainly become a standard work dealing with molecular rearrangements. The writer of the review has always looked with doubt on the Fischer acyl migration and its extension by Perkin, and has given voice to his objections. The fact that Professor Porter has omitted this phenomenon tacitly supports this opinion.

M. NIERENSTEIN.

CONTEMPORARY DEVELOPMENTS IN CHEMISTRY. New York: Columbia University Press; London: Oxford University Press. Price 55s.

The volume under review is a collection of lectures given at Columbia University during the summer session of 1926, on the occasion of the Chandler Chemical Laboratories being opened. These lectures were delivered by some of the most famous American and European chemists, including Sir James Irvine, of St. Andrews. Each lecture is in itself a summary of highly specialised work, and a variety of subjects treated includes the Chemistry of Odorous Compounds by M. T. Bogert, Chemical Reactivity by T. F. Norris, the Rare Gases by R. B. Moore, Radicals as Chemical Individuals by C. A. Kraus, and the Periodic Table by B. S. Hopkins. Altogether twenty-five lectures are embodied in this remarkable collection.

Out of patriotism, special reference must be made to the two lectures by Sir James Irvine, the only representative of Great Britain. In these Sir James gives a summary of his classical researches on the carbohydrates, to which he has devoted a life time. Many other workers have followed in his footsteps, but it must always be remembered that the elucidation of sugar chemistry is due to the two outstanding leaders in this field of research, Emil Fischer and J. C. Irvine. Their names will remain as permanent landmarks in the history of Chemistry.

In addition to the two lectures dealing with carbohydrates, the book contains much material which can strongly be recommended to the student of chemistry.

M. NIERENSTEIN.

COLLOID CHEMISTRY—THEORETICAL AND APPLIED. By Selected International Contributors. Collected and Edited by JEROME ALEXANDER. Volume II. **BIOLOGY AND MEDICINE.** Pp. 1029. New York: The Chemical Catalog Company, Inc. 1928. Price \$15.50.

This is the second volume of Alexander's remarkable compilation of papers by international authorities on pure and applied Colloid Chemistry. Fifty-seven chapters deal with a wide range of material bearing on biochemistry, physiology and medicine. The status of the volume is evidenced by the contributions of such scientists as Sir William Bragg, Wolfgang Pauli, G. Bredig, Andor Fodor, H. Schade, Du Noüy, Jacques Loeb—to name but a few.

The editor (with C. B. Bridges) opens with a long paper on "Some Physico-Chemical Aspects of Life, Mutation and Evolution." This is as full of interest to the colloid chemist as to the biologist. Related papers are "The Colloidal Systems of the Living Organisms" (Bottazzi), "The Physical Properties of Protoplasm" (Seifriz), "Protoplasm" (Heilbrunn), "The Colloidal Structure of Protoplasm and Protoplasmic Action" (Lillie), "The Physical Basis of Life" (Wilson). The botanist and bacteriologist, too, are catered for in contributions of a specialised character.

The magnitude of the volume forbids detailed notice of all the papers. Several, however, sum up the present position of research and knowledge in readable and authoritative fashion. Bragg briefly surveys the task of applying the new X-rays analysis to colloidal systems. "The X-rays can find something to measure even in the substances that most seem to deserve the title of amorphous." The problem of the ageing of colloids is discussed by Rocasolano, who briefly recapitulates his research on the variations in viscosity, surface tension, electric charge and conductance in colloid systems. Dhar and Chakravarti have an important communication on "Hydration and Viscosity of Sols in the Presence of Electrolytes." Surface tension measurements and magnitudes are treated in several papers, Bottazzi, in particular, giving very clear data regarding the isoelectric point in relation to surface tension. His paper is critical of others and well supported by his own data.

Yoe has two useful articles: "Nephelometry" and "Colorimetry," both summarising present technique and knowledge in these fields.

"Proteins as Colloids," by W. Pauli, is a masterly contribution, and is followed by a lucid summary by Fischer of his well-known work, in his paper "Lyophilic Colloids and Protoplasmic Behaviour." Brailsford Robertson's familiar views regarding the combination of proteins with acids and bases are given in a long paper which should be read in relation to the appendix to the book: Loeb's Pasteur Lecture of 1922 on "The Explanation of the Colloidal Behaviour of Proteins." Spiegel-Adolf discusses the physical chemistry of the heat-denaturation of proteins, a subject of profound importance in colloid-bio-chemistry.

Enzymes are treated by several authors. Medicine receives very full discussion, and the outstanding contribution is Schade's "Colloid Chemistry and

Internal Medicine," a subject already associated with the author's name. The medical papers are by specialists world-famous in their fields, as, for example, Kahn on "Serum Diagnosis of Syphilis." Lobar pneumonia, cancer, acute inflammatory process, external superficial burns, concretions, tuberculosis, dust hazard, and the therapeutics of colloids, are dealt with in valuable papers. The colloid chemist even proposes a new theory of vitamins, von Hahn again presenting his views on the vitamin-containing substances, that these act not because of a chemically definable constituent, but because of their inherent surface or capillary activity.

Alexander has done a great service to all interested in Colloid Chemistry. Every field of modern scientific research reacts to progress in the study of colloidal systems, and in the present volume it becomes abundantly evident that the organic chemist, biochemist, physiologist and medical practitioner, must, if he keeps up-to-date, follow the new implications and applications of colloid studies in his own subject.

The book is printed, illustrated and bound in commendable fashion, and printing errors are few. As a store of information and as a summary of modern work it will take its place in all laboratories where colloid study has any part in teaching or research.

WILLIAM CLAYTON.

Publications Received.

INDUSTRIAL CARBON. By C. L. MANTELL. London: Chapman & Hall. Price 21s. net.

BACTERIOLOGY. By F. W. TANNER. London: Chapman & Hall. Price 22s. 6d. net.

RECENT ADVANCES IN HAEMATOLOGY. By A. PINEY. London: J. & A. Churchill. Price 12s. 6d.

DIZIONARIO DI MERCEOLOGIA E DI CHIMICA APPLICATA. 5 Ed. Vol. I. (A to C). Price Lire 60.

A POCKET BOOK FOR CHEMISTS. By T. BAYLEY. 9th Edition. E. & F. N. Spon, Ltd. Price 8s. 6d. net.

TREATISE OF INORGANIC AND THEORETICAL CHEMISTRY. Vol. IX. By J. W. MELLOR. Longmans. Price 63s. net.

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, April 3rd, the President, Mr. Edward Hinks, being in the chair.

Certificates were read for the first time in favour of:—Alfred Norman Leather, B.Sc., F.I.C., Richard Harold Morgan, B.Sc., A.I.C., and William George Painton, B.Sc., A.I.C.

Certificates were read for the second time in favour of:—Peter Trevisa Clarke, B.A., Alfred Clive James, B.Sc., A.I.C., Herman Lee, B.Sc., A.I.C., James Frederick Morse, Lawrence John Odling, Willie Horner Wilkinson.

The following were elected Members of the Society:—Frank Atkins, Edmund Baron Bennion, M.Sc., A.I.C., John Haslam, M.Sc., A.I.C., Stanley Gordon Kendrick, B.Sc., A.I.C., Bryn Jones, B.Sc., A.I.C., John Upton Lewin, B.Sc., A.I.C., and Leslie John Walker.

The following papers were read and discussed:—"Furfural and Diastase in Heated Honey," by L. H. Lampitt, D.Sc., F.I.C., E. B. Hughes, M.Sc., F.I.C., and H. S. Rooke, M.Sc., A.I.C.; "Further Notes on Methods of Sewage and Water Analysis; Anti-Oxidation and Stabilisation of Pollution," by J. W. Haigh Johnson, M.Sc., F.I.C.; and "Potassium Cyanate as a Reagent for the Detection of Cobalt," by B. J. F. Dorrington, B.Sc., A.I.C., and A. M. Ward, B.Sc., Ph.D., A.I.C.

Obituary.

GEORGE WATSON GRAY.

By the death of George Watson Gray, which occurred on the 12th February last, at the age of 66, Liverpool has lost one of its best known consulting chemists. He received his early training at the Rutherford Technical College, Newcastle-on-Tyne, and in the laboratories of Mr. John Pattinson, and came to Liverpool in 1883 as

assistant to Mr. A. Norman Tate. Ten years later Mr. Watson Gray set up his own laboratories and continued in practice until a short time before his death.

Among the branches of analytical work to which he devoted special attention may be mentioned the rarer constituents of alloy steels, ferro-silicon, and tanning materials, and he was the author of many papers dealing with these matters, latterly in collaboration with his partner, Mr. James Smith.

Mr. Watson Gray took an active part in the establishment in Liverpool of the first provincial Section of the Institute of Chemistry, and occupied the chair for the first few years. Until ill-health interfered he was an extremely hard worker; he used to say that his work was his hobby, but he found time occasionally for a tramp in the Lake District, of which he was very fond.

He was a Member of the Society of Public Analysts for over forty years.

E. GABRIEL JONES.

The Freezing Point of Milk.

By A. VAN RAALTE, D.Sc.

FOR more than twenty years we have made use of the freezing point of milk to determine with certainty its adulteration with water. Milk which has a freezing point nearer to zero than -0.53° C. is, as we are convinced, adulterated.

So far back as 1898 the late Dr. A. Lam regularly used this method in his laboratory in Rotterdam, so that the method has been in use more than 30 years in this country. In the *Journal of the Dutch Society for the Investigation of Milk* he published, in 1909, an article on the freezing point of milk. He cited there 33 different articles, published between 1892 and 1909, dealing with this method; all the authors gave for the freezing point of milk figures varying between -0.54° and -0.59° C.; only Messrs. Bordas and Genin (1896) gave figures between -0.46° C. and -0.56° C., but they analysed—without knowing it—some adulterated samples. The figures, given by Mr. Winter in 1895, viz. -0.54° C. to -0.57° C., have proved to be correct.

Dr. Lam came to the conclusion that mixed milk with a freezing point nearer to zero than -0.54° C. must contain added water; and that milk with a freezing point lower than -0.59° C. must be considered as unsatisfactory.

The milk of some individual cows may sometimes give abnormal figures, but the determination of the freezing point in thousands of samples of mixed milk, taken in the presence of inspectors, has shown that this point lies between -0.54° C. and -0.57° C. I, myself, in 1909, when analysing 155 samples of milk, taken in the presence of inspectors, obtained figures for the freezing point varying only between -0.54° and -0.57° C.

Even in 1914, however, there was still a difference of opinion between some Dutch experts on this subject. But after the polemical discussions of that year

all Public Analysts in Holland agree that normal mixed milk has a freezing point between -0.54° and -0.57° C.

Ever since, all competent judges in Holland have regarded milk with a freezing point nearer to zero than -0.54° C. as being adulterated with water, and the Dutch Government has fixed in its Milk Decree the maximum for the freezing point at not higher than -0.53° C., to be absolutely on the safe side.*

It is, of course, understood that the acidity of milk, when being analysed, may not exceed 9 (c.c. of $N/4$ alkali for 100 c.c. of milk, with phenolphthalein as an indicator).

Milk obtained from cows with diseased udders can have a freezing point below -0.57° C. Such milk contains, while still in the udder, a great number of lactic acid germs; so long as the milk remains in the udder all lactic acid will be neutralised, as was proved by Mr. Straub in my laboratory. Immediately after milking lactic acid will be formed. This lactic acid does not manifest itself in a high acidity; the acidity of this milk is normal, because milk of such cows has a very low acidity (± 4) immediately after milking.

In most cases the low freezing point makes it unnecessary to take samples in the presence of inspectors, and this method is very rapid in the hands of a skilled analyst. This is a great advantage. The results of the control of milk are largely dependent upon close supervision.

It is for this reason that, in Amsterdam, we analyse every year about 30,000 samples of milk, *i.e.* about one sample for every thirty inhabitants.

Thanks to this strict control it has been found possible to obtain a figure of only 2 per cent. of milk samples adulterated with water, as was the case in 1927. In that year we analysed 29,124 samples, of which 596 contained added water.

In order not to give an advantage to the skilled adulterator it is necessary to determine the freezing point of any milk with a percentage of non-fatty-solids of 8.2 and less, excepting during summer, when we take 8 per cent. as the limit.

This made it necessary in 1927 to determine the freezing point of 1876 samples, an average of 6 a day.

This number, of course, may vary; we determined the freezing point of a maximum of 12 samples a day, and this was done by the same chemist, with an assistant, who analysed 100 samples of milk, and generally had to analyse several samples of butter-milk on the same day.

* The following note from the Report of Dr. Monier-Williams deals with the confusion which may arise from the use of the terms "higher" and "lower" as applied to freezing points below zero:—"A freezing point of -0.520° is obviously higher than one of -0.550° , but it is apparently the usual custom among writers on the subject to express the results obtained in terms of the *depression* of the freezing point with reference to water, generally expressed by the symbol Δ . Thus a value of 0.550° would be higher than one of 0.520° , as representing a greater depression of the freezing point. The adoption of the latter mode of expression has much to recommend it and tends to avoid confusion as the terms 'higher' and 'lower' correspond with the actual figures and the constant repetition of the minus sign is avoided. In the present report therefore the symbol Δ is used throughout to indicate the difference between the freezing point of milk and that of water."—EDITOR.

With reference to the two excellent papers published in the March issue of *THE ANALYST*, it may be mentioned that some of the questions raised in the discussion have been answered in the following contributions from my laboratory: J. Straub, "Milchsäurebestimmungen in Milch" *Rec. Trav. Chim. Pays Bas*, 1927, **46**, 866), and J. Straub and L. Soep, "Recherches sur la Concentration osmotique des Lumeurs" (*Arch. néerland. de Physiol. de l'Homme et des Animaux*, 1928, **12**, 346).

The freezing point method is now coming into use in the United States and in Germany. Figures found in both countries are in absolute conformity with the figures we find in Holland.

The method of the freezing point of milk therefore deserves international acceptance.

KEURINGSDIENST VAN WAREN,
732 KEIZERSGRACHT,
AMSTERDAM.

The Determination of Small Quantities of Beryllium in Rocks.

By B. E. DIXON, M.Sc., A.I.C.

(Read at the Meeting, February 6, 1929.)

THERE is a good deal of negative evidence for the supposition that the occurrence of beryllium in small quantities is much more extensive than appears from its infrequent mention in mineral and rock analyses. Normally, beryllium is not tested for in these circumstances, and is then probably included in the figure for aluminium. Absence of distinctive qualitative tests for beryllium to some extent accounts for this. Examination of those analyses which are provided with a description of the method employed has led to the conclusion that the beryllium figure is, in many cases, untrustworthy. This is chiefly due to the lack of an accurate and suitable method for separating beryllium from titanium; this problem seems to have been overlooked, although there are a number of excellent methods available for separating beryllium from aluminium. In view of this fact, and because it is highly probable, from mineralogical considerations, that titanium will be present in appreciable quantities in rocks containing small quantities of beryllium, an attempt has been made to devise a suitable separation of these two elements.

Most treatises on mineral analysis recommend that beryllium should be separated by the method of Parsons and Barnes (*J. Amer. Chem. Soc.*, 1906, **28**, 1589), which depends upon the total solubility of beryllium hydroxide, and the

total insolubility of ferric and aluminium hydroxides in boiling 10 per cent. sodium bicarbonate solution. In these circumstances, however, titanium is not completely precipitated. For example, a solution containing 0.0252 grm. of titanium chloride and 0.0248 grm. of beryllium chloride was treated according to the method of Parsons and Barnes; only 0.0219 grm. TiO_2 was precipitated, the remainder being found with the beryllium. This is probably due to the formation of a soluble double alkali titanium carbonate (Auger, *Compt. rend.*, 1923, 177, 1302), which is not wholly reprecipitated under the conditions of the experiment.

In other cases the titanium has been separated from, *inter alia*, beryllium, by precipitating the titanium either with hydrogen sulphide in boiling acid solution (e.g. Glaser, *J. Amer. Chem. Soc.*, 1896, 18, 782), or by pouring into sodium hydroxide solution and boiling (Wenger and Wuhrmann, *Ann. Chim. anal.*, 1919, 1, 337). Both methods are open to grave risk of contamination of the titanium precipitate with beryllium, and the latter method has the further disadvantage that titanium hydroxide is markedly soluble in the alkaline solution (Hillebrand, "Analysis of Silicate and Carbonate Rocks," p. 132). Nor are these objections removed if sodium peroxide is used in conjunction with the alkali (Noyes and Bray, "Qualitative Analysis of the Rare Elements," p. 165).

USE OF ORGANIC BASES AS REAGENTS.—After some preliminary search, it was decided that the most promising method of accomplishing a separation of titanium and beryllium seemed to be one involving the use of organic bases. The use of various organic bases for the precipitation of hydroxides of some of the rarer elements has been described by Jefferson (*J. Amer. Chem. Soc.*, 1902, 24, 540), and Hartwell (*id.*, 1903, 25, 1128). Hess and Campbell (*id.*, 1899, 21, 776) introduced the use of phenylhydrazine for the quantitative precipitation of aluminium, and the scope of this reagent was widened by Allen (*id.*, 1903, 25, 421), who worked out separations of aluminium, titanium, zirconium, and thorium from ferrous iron and beryllium, which are not precipitated by phenylhydrazine. It was found (see later) that phenylhydrazine was not suited to the separation of beryllium and titanium, chiefly because some of the beryllium tends to be precipitated with the titanium. It was thought that, if a base could be found, sufficiently weak to avoid causing any precipitation of the beryllium, whilst still strong enough to precipitate completely the very weak hydroxide of titanium, a successful separation might be worked out. After numerous trials such a reagent was found in *p*-chloroaniline, which possessed certain other advantages. A series of tests was carried out to ascertain how far the separation was complete, and for this purpose specially pure standard solutions of beryllium and titanium chlorides were prepared.

SEPARATION BY MEANS OF *p*-CHLOROANILINE.—Known volumes of standard titanium and beryllium chloride solutions were measured out into a beaker and the strongly acid mixture diluted to 250 ml. and heated nearly to boiling point. Ammonium hydroxide was then added cautiously with constant stirring until the solution acquired a turbid appearance, but was still distinctly acid to litmus.

The process of neutralisation, which is very critical, should not be carried to the point where a perceptible flocculation takes place. From 1 to 1.5 grm. of *p*-chloroaniline were then added, the cover-glass replaced to avoid loss by spraying, and the solution carefully brought to boiling point and maintained at this temperature for three minutes. The solution was filtered, the precipitate washed with hot water until free from chloride, ignited and weighed. The filtrate from the titanium was heated, a slight excess of ammonium hydroxide added,* the solution boiled for a moment and filtered. The precipitate of beryllium hydroxide was washed with dilute, slightly ammoniacal ammonium nitrate solution until free from chlorides, ignited and weighed. Any deposit adhering to the sides of the beaker was dissolved in dilute nitric acid, precipitated with ammonia, and added to the main beryllium precipitate.

TABLE I.

No.	Amounts taken (in grm.)		Amounts found (in grm.)		Error (in grm.)	
	BeO.	TiO ₂ .	BeO.	TiO ₂ .	BeO.	TiO ₂ .
1	0.0056	0.0020	0.0057	0.0019	+0.0001	-0.0001
2	0.0052	0.0471	0.0052	0.0473	nil	+0.0002
3	0.0052	0.0471	0.0051	0.0472	-0.0001	+0.0001
4	0.0052	0.0471	0.0050	0.0475	-0.0002	+0.0004
5	0.0052	0.0471	0.0051	0.0470	-0.0001	-0.0001
6	0.0212	0.0056	0.0212	0.0055	nil	-0.0001
7	0.0212	0.0056	0.0213	0.0055	+0.0001	-0.0001
8	0.0198	0.0107	0.0201	0.0106	+0.0003	-0.0001
9	0.0198	0.0107	0.0198	0.0107	nil	nil
10	0.0409	0.0056	—	0.0061	—	+0.0005
11	0.0409	0.0056	—	0.0060	—	+0.0004
12	0.0409	0.0056	—	0.0056	—	nil
13	0.0409	0.0056	—	0.0058	—	+0.0002
14	0.0409	0.0056	—	0.0058	—	+0.0002
15	0.0409	0.0056	—	0.0055	—	-0.0001

It is evident that, with quantities of beryllium and titanium of the order indicated in Table I., a second precipitation with *p*-chloroaniline is unnecessary. It should also be avoided, if possible, owing to the difficulty of redissolving in acid the precipitate of titanium after it has been boiled for three minutes. Moreover, no titanium could be detected by means of hydrogen peroxide in the beryllium residues.

If the separation of titanium and beryllium by means of *p*-chloroaniline is carried out in a solution containing a considerable quantity of sulphuric acid instead of hydrochloric acid, the same accuracy is not attained. The error is insignificant when only small quantities of beryllium are present, but if the beryllium content is increased it is found that the titanium figure is too high (Table II). Since precautions were taken to decompose by ignition with ammonium carbonate

* At this point, if the correct acidity for the titanium separation had been attained, at least 1.5 ml. 4 *N*-ammonium hydroxide solution were required before the first appearance of a precipitate.

any sulphate that might have been present in the titanium precipitate, this increase in weight must be due to beryllium.

TABLE II.

No.	Amounts taken.			Amounts found.		Error.	
	BeO. Grm.	TiO ₂ . Grm.	Total. Grm.	BeO. Grm.	TiO ₂ . Grm.	BeO. Grm.	TiO ₂ . Grm.
1	0.0058	0.0481	0.0539	0.0058	0.0482	nil	+0.0001
2	0.0058	0.0481	0.0539	0.0052	0.0488	-0.0006	+0.0007
3	0.0483	0.0502	0.0985	0.0463	0.0518	-0.0020	+0.0016

USE OF PHENYLHYDRAZINE PRECIPITANT.—In order to compare the value of the two organic precipitants for this purpose, a series of tests was carried out as described above, but with the substitution of phenylhydrazine for *p*-chloroaniline. The results are tabulated in Table III.

TABLE III.

No.	Amounts taken.			Amounts found.		Error.	
	BeO. Grm.	TiO ₂ . Grm.	Total. Grm.	BeO. Grm.	TiO ₂ . Grm.	BeO. Grm.	TiO ₂ . Grm.
1	0.0058	0.0460	0.0518	0.0050	0.0467	-0.0008	+0.0007
2	0.0058	0.0460	0.0518	0.0052	0.0465	-0.0006	+0.0005
3	0.0061	0.0471	0.0532	0.0056	0.0477	-0.0005	+0.0006
4	0.0061	0.0471	0.0532	0.0055	0.0478	-0.0006	+0.0007

Comparing these figures with the corresponding tests 2-5, Table I, with *p*-chloroaniline, it is seen that, when phenylhydrazine is used, the error involved is appreciable. This probably indicates that phenylhydrazine is a sufficiently strong base to precipitate some beryllium with the titanium. A second precipitation, which might eliminate this beryllium, has the drawbacks of unduly lengthening the time of analysis and the difficulty of redissolving the titanium precipitate already referred to. Further, even when freshly made, phenylhydrazine forms an appreciable amount of tarry matter which may occlude beryllium compounds that cannot then be washed out. This tar formation can be decreased by maintaining the solution at a lower temperature, but only at the sacrifice of further contamination of the titanium hydroxide. *p*-Chloroaniline is free from these disadvantages.

OBJECTIONS TO THE USE OF TANNIC ACID.—Moser and Singer (*Monatsh.*, 1927, 48, 673) state that titanium can be quantitatively separated from beryllium by precipitation with tannic acid in the presence of acetic acid and large quantities of ammonium acetate and nitrate. Iron can be separated from beryllium in the same manner, but in this case a little hydrogen peroxide is added to the solution because the tannic acid always reduces some of the iron to the ferrous state. It is doubtful, however, if hydrogen peroxide could be employed in the presence of titanium. Moreover, when iron is present, the acidity of the solution has to be

reduced to such an extent as to favour co-precipitation of some of the beryllium with the iron (and titanium, if this be present). Since a small quantity of iron almost invariably accompanies the beryllium and titanium in the final stages of the method of analysis to be described, the use of tannic acid here is excluded for the reasons just mentioned. The use of cupferron (Lundell and Knowles, *J. Amer. Chem. Soc.*, 1920, 42, 1439) in this connection is limited, because of the errors and loss of time introduced by the complete destruction of the excess reagent that is necessary before the small quantity of beryllium present can be determined in the filtrate from the titanium.

DETERMINATION OF SMALL AMOUNTS OF BERYLLIUM.—When it is of importance to make an exact determination of small amounts of beryllium in, for example, a silicate rock, the following procedure is suggested as an alternative to that usually followed in the treatment of the precipitate formed by ammonia in the presence of ammonium chloride. This precipitate should contain the iron, aluminium, titanium, beryllium and phosphorus, with small amounts of chromium, zirconium, vanadium, if present, and residual silica. The use of sodium carbonate in the fusion of the mixed oxides at this stage (Wenger and Wuhrmann, *loc. cit.*, and Britton, *ANALYST*, 1922, 47, 50) has the advantage of (1) avoiding the introduction of the sulphate ion, (2) removing the residual silica in a form in which it can be readily estimated, and (3) eliminating phosphorus, which might be troublesome later. The subsequent treatment by sodium bicarbonate removes the iron, and much of the titanium, and the final separation by *p*-chloroaniline removes the remainder of the titanium, leaving the beryllium in solution. If present, chromium dissolves in the extract of the sodium carbonate melt together with the aluminium; vanadium, which would behave similarly, is not likely to be present in rocks containing beryllium. Traces of zirconium which may dissolve in the sodium bicarbonate solution are completely precipitated by *p*-chloroaniline. If much iron is present in the original mixed oxides, traces may escape the double sodium bicarbonate precipitation, but these also are completely precipitated by *p*-chloroaniline.

Method.—The hydroxides of iron, aluminium, etc., are separated from the solution of chlorides by two precipitations of the boiling solution with ammonia, followed by an evaporation of the ammoniacal filtrate to recover traces of these metals which have escaped precipitation. The united precipitates are placed in the weighed platinum crucible containing the residue from the silica determination, dried, ignited and heated until of constant weight. The contents of the crucible are ground with a platinum rod and intimately mixed with 5 grms. of sodium carbonate (prepared by heating pure sodium hydrogen carbonate), a thin layer of carbonate being spread on the top. The crucible is then heated for 2½–3 hours at a temperature just high enough to keep the contents molten. The cooled melt is left to digest overnight in 500 ml. water, passed through a fine filter and washed with dilute sodium carbonate solution. If it is intended to estimate the aluminium gravimetrically, the fusion process is now repeated.

If chromium is present, it can be estimated colorimetrically in the filtrate after the bulk of the solution has been somewhat reduced by evaporation. The solution is then carefully acidified with 15 ml. of hydrochloric acid, and evaporated to dryness in a platinum basin to render the small amount of silica present insoluble. The basin is drenched with a few ml. of hydrochloric acid, 100 ml. hot water added and the solution filtered. The precipitate is ignited and weighed in a platinum crucible and the weight of silica determined by the loss in weight after evaporation with hydrofluoric and sulphuric acids. If desired, aluminium can be determined in the filtrate by a double precipitation with ammonia; correction must be made for the chromium and phosphorus which are also precipitated.

Ten ml. of hydrochloric acid are poured into the crucible in which the sodium carbonate fusion took place, in order to extract any adhering matter, and the extract is used to dissolve the precipitate of iron, titanium, and beryllium on the filter paper. The filter paper is ashed and any residue formed dissolved in hydrochloric acid and added to the main solution. The solution is now treated according to Parsons' and Barnes' process (*loc. cit.*). The solution is neutralised with ammonia and 10 grms. of solid sodium bicarbonate (free from sodium carbonate) per 100 ml. of solution are added to the cold solution. The beaker is covered with a clock-glass and the solution heated to boiling as quickly as possible and maintained at boiling point for one minute. The solution is quickly cooled and filtered. The residue is washed with 50 ml. of hot 10 per cent. sodium bicarbonate solution, redissolved in hydrochloric acid, neutralised as before, and the precipitation with sodium bicarbonate repeated. The final precipitate of ferric and titanium hydroxides is ignited in the platinum crucible which was used for the sodium carbonate fusion.

The united filtrates from the precipitations by sodium bicarbonate are carefully acidified with 30 ml. hydrochloric acid, and the solution boiled to expel carbon dioxide. In view of the large amount of sodium salt present, a preliminary separation of the beryllium and titanium hydroxides from the solution is advisable. The precipitate is dissolved in hydrochloric acid and the treatment with *p*-chloroaniline as described on page 270 is applied. The precipitate from the *p*-chloroaniline is redissolved in hydrochloric acid and the precipitation process is repeated. The beryllium is determined in the united filtrates by precipitation with ammonia, and the precipitate, after ignition and weighing, is tested for contamination with iron or titanium.

The precipitate produced by the *p*-chloroaniline is added to the platinum crucible containing the bulk of the iron and titanium and ignited. The contents of the crucible are brought into solution by fusion with potassium pyrosulphate and subsequent leaching with dilute sulphuric acid. In this solution the titanium and iron can be estimated by suitable methods, for example, the titanium colorimetrically and the iron by means of titanous chloride. The crucible is weighed empty, and dissolved platinum is separated from the solution by means of sulphuretted hydrogen, in order to arrive at the correct total weight of oxides precipitated by ammonia. The weight of alumina, if it has not been directly

determined, is found by subtracting from the total the weights of all other oxides.

Table IV shows the results obtained in the determination of beryllium by the method just described in mixtures of known amounts of iron, aluminium, titanium, and beryllium chlorides. In the case of numbers 3 and 4 the precipitate from the *p*-chloroaniline was not subjected to a second precipitation by that base. With these two exceptions it is seen that the results are in excellent agreement with the theoretical. Examination of the beryllium residues showed them to be free in every case from titanium and iron.

TABLE IV.

No.	Amounts taken.				Found.	Error.
	Fe ₂ O ₃ . Grm.	Al ₂ O ₃ . Grm.	TiO ₂ . Grm.	BeO. Grm.	BeO. Grm.	
1	0.0270	0.0258	0.0248	0.0250	0.0248	-0.0002
2	"	"	"	"	0.0254	+0.0004
3	"	"	"	"	0.0243	0.0007
4	"	"	"	"	0.0233	-0.0017
5	0.1082	0.1032	"	"	0.0252	+0.0002
6	"	"	"	"	0.0249	-0.0001

SUMMARY.—(1) It is suggested that the chief obstacle to the accurate determination of small quantities of beryllium in silicate rocks lies in the difficulty of its separation from titanium.

(2) A method is described for the separation of beryllium and titanium by means of *p*-chloroaniline.

(3) Details are given of a method for the analysis of a silicate rock with especial reference to the accurate estimation of beryllium in small quantities.

The author desires to express his thanks to Sir Robert Robertson for permission to publish this paper, and also to Dr. J. J. Fox for his valuable criticism.

GOVERNMENT LABORATORY,
LONDON, W.C.2.

New Apparatus for Electrolytic Analysis.

By HENRY J. S. SAND, D.Sc., Ph.D., F.I.C.

THE apparatus to be described is based, in general purpose and design, on that used by me in 1907 (*J. Chem. Soc.*, 1907, **91**, 374), and in later years for the deposition and separation of metals by electrolysis. The apparatus has been modified by several users of the methods described by me and of similar ones (Fischer, *Z. Elektrochem.*, 1907, **13**, 469; and *Elektroanalytische Schnellmethoden*, Stuttgart, 1926; Lassieur, *Electroanalyse Rapide*, Paris, 1927). The subsequent designs have been superior in economy of platinum, but I believe have been inferior in ease

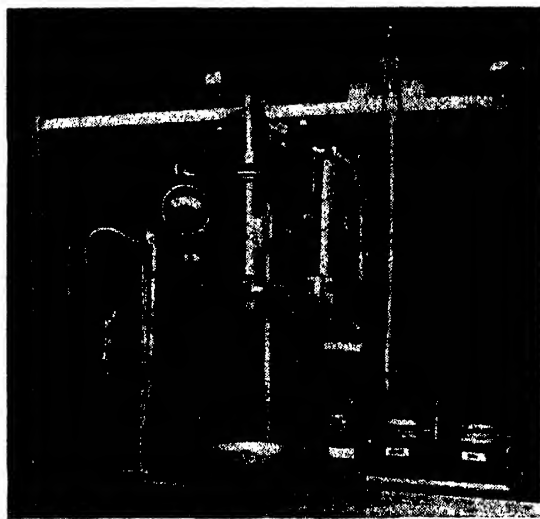


Fig. 1.

and rapidity of working. In 1911 (*Trans. Faraday Soc.*, 1911, **6**, 205) I also described apparatus for the deposition of certain metals, in which the anode was mounted on glass and the cathode constructed of metals such as silver and nickel. The designs of electrodes now submitted are developments of these, having as their main object a reduction in the weight of platinum required. The stand and other auxiliary apparatus have also been completely redesigned in detail, but the following distinctive features, to which importance is attached, are either the same as, or developments of, those to be found in the old design.

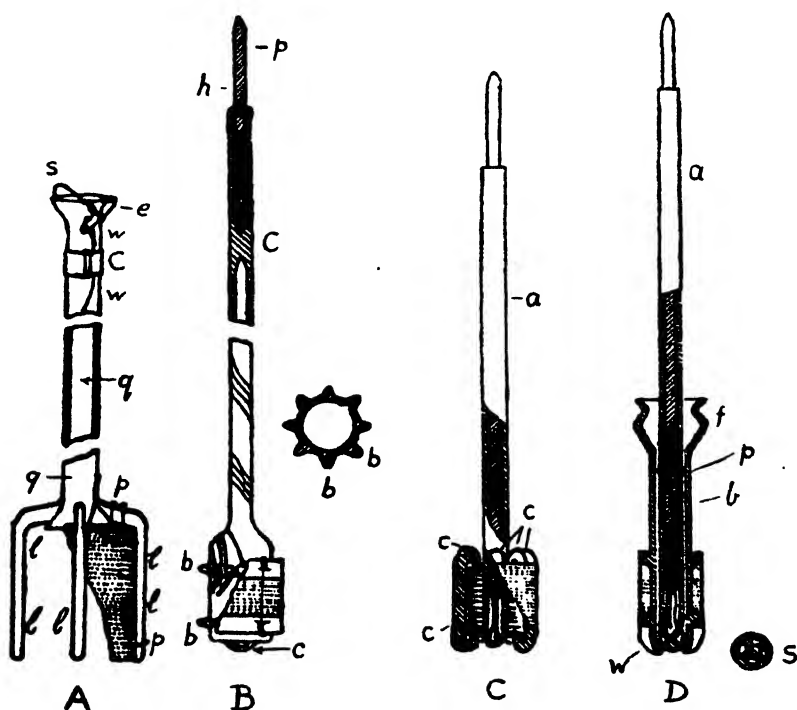
The outer electrode surrounds the inner everywhere, except below, being placed as close as possible to the bottom of the beaker. This is of importance when it is desired to confine the lines of flow of the current to the space between the electrodes for the purpose of controlling the potential of the outer. The stem of the

inner electrode revolves inside a quartz glass guide tube which forms an integral part of the outer, thus ensuring correct alignment, even when the clearance between the two electrodes is reduced to a minimum. The process of washing and disconnecting is made as rapid as possible by the following features. The support for the beaker can be removed without interfering with the position or connections of the electrodes, and the outer may be washed with a spray of water while the beaker is being lowered. Disconnection is carried out by loosening a clamp which holds the outer electrode and simply pulling the inner out of a specially designed clutch which forms part of a flexible rubber spindle. The two electrodes may be removed together without a short-circuit between them, if only the inner one is held by its stem, and they are suitable for washing by immersion in alcohol or other drying liquids contained in jars. Since the quartz guide tube now forms part of the outer electrode, a fixture must be provided for drying it with hot air. This is illustrated in Figure 5B and also in Figure 1, and consists of a quartz drying tube which swings in a brass fork *f* attached to the back of the board *a* (Fig. 1). The electrode is placed on the end *a*, while the portion *b* is heated by means of a Bunsen flame, air being blown at the same time through the end *c* by means of a hand spray bellows. A preliminary drying of the gauze of the electrode thus also takes place, which is then completed by holding the burner under the electrode itself at some distance from it.

THE ELECTRODES.—Both electrodes are usually mounted on quartz glass frames, but ordinary glass may often be used for the inner one, when it has not to be weighed. In some cases a frame constructed of rubber and glass has likewise been found useful. A rotating anode is also described which is designed to be used in conjunction with a revolving partition consisting of a parchment paper thimble. This is a development of the anode described by me (*J. Chem. Soc.*, 1908, **93**, 1589). The electrodes are shown in Figure 2, *A* representing the outer, *B* the inner mounted on a quartz glass frame, *C* the same mounted on a rubber plus glass frame, whereas *D* represents the revolving anode designed for use with a parchment diaphragm. The frame of the outer electrode is built up on a quartz glass tube *q*, of about 7 mm. bore, which is flared at both ends; about 2 mm. from the lower end are sealed four legs *l*, of which three are shown. These are made from 4 mm. rod, the horizontal portions being flattened to give additional strength. The top of the tube *q* is provided with two eyelets *e*, which serve as supports for a suspension wire *s*, and also provide a means for holding the leading-in wire in position. The platinum gauze jacket, which is shown partly cut away, is provided with a small slit at the top to allow it to be drawn over the flange, left at the bottom of the flared quartz tube, and is then fastened firmly to the frame by means of thin platinum wire. In addition, clips of thin platinum wire *p*, twisted together over the legs of the frame, hold the jacket firmly in position. A leading-in wire *w*, of 0.4 to 0.6 mm. diameter, connects the gauze jacket in a steep spiral with the collar *c*, and is held in position by the eyelet *e*. The collar, which is designed to be held by a clamp, is made of thin foil or gauze, the ends being folded together as shown.

If from one cause or another one of the legs of this electrode should become fractured, it is a simple matter to remove the platinum and repair the frame in the oxy-gas blowpipe. For this purpose a small stand should be improvised. It should be built up on a suitable base to have a central rod for holding the tube, and outside this a block of wood covered with uralite, having a hole of the correct size to take the leg. By successively adjusting all the legs to fit into this hole, while the tube is supported by the central rod, a true position for all the legs may be ensured.

Fig 2



The frame of the inner electrode *B* is a closed pipette-shaped vessel provided with two rows of eight beads, *b*, on the body of the frame (shown also in section). The stem is a tube which is closed at *C*, its diameter being about 1.5 mm. smaller than the bore of the tube *q* of the outer electrode, in which it is designed to revolve. About three cm. of the stem are left open at the top, to provide a seating for the leading-in peg *p* of the electrode, made of non-corrodible metal, preferably of silver. The latter is partly cut away to provide space for it to be cemented to the tube, ridges equal to the bore of the tube being left to ensure a central position.

It has been found that if lead (grain) is melted in the tube, heated to dull red heat, and the peg, likewise heated to dull red heat, is then introduced, a perfectly satisfactory joint is made on cooling. The peg has a hole of about 1 mm. diameter immediately above the quartz tube. The connection between the platinum gauze jacket of the electrode and the peg is made by 0.3 mm. platinum wire, which is wound upwards on the exterior of the stem in four steep spirals. For this purpose the wire is first wound round the body of the frame below the top row of beads, two short branch wires from it having been previously provided by twisting it on itself for about 1 cm. From the loop formed below the beads the wire is taken past one of the beads in a steep spiral to the top of the stem. It is then threaded through the hole *h* in the peg, and taken down again in a similar parallel spiral. At the foot it is taken past one of the beads and twisted to the free end of the loop or to a branch wire, then taken spirally again to the top, and back as before, being finally secured to one of the branch wires. In order to ensure good contact between the platinum wire and the silver peg, a small silver wire wedge is driven into each end of the hole *h*. The jacket consists of a piece of gauze which is strengthened by means of foil at the top and bottom edges, where it is to be supported on the beads. The other edges are finished off in such a way as to allow the jacket to be pulled tightly over the beads as a cylinder by means of pieces of platinum wire. The jacket is also provided with two wires which are brought into contact with the leading-in wires, by being twisted to the free branches mentioned above. The electrode can be hung from a balance by means of the quartz glass loop.

When the electrode is made of ordinary glass the construction is somewhat modified. The leading-in rod, usually of aluminium, is taken down the whole of the stem into the body of the frame, and is cemented in position with a red lead cement. Four platinum wires are fused into the aluminium and sealed through the body of the frame, which resembles that described for quartz. Also, for glass it was sometimes found useful to take a single wire spirally up the outside of the stem to prevent it from being chafed by contact with the guide tube of the outer electrode.

The electrode *C* was found very useful as an anode for zinc and similar determinations. It is built up on a glass tube into which an aluminium rod carrying four platinum wires is cemented. These wires are taken through the glass tube at the bottom, as shown. This is most simply accomplished by cutting the tube at the place where the wires leave it, placing these in position, and then sealing on the cut portion again, drawing off, and finally closing the tube at the place shown. Over the glass tube is slipped a piece of thick-walled rubber tubing or a rubber plug, made of black rubber (*i.e.* free from metal oxides). This serves as a support for eight hooks, *c*, made of glass rod. On these is mounted the jacket of platinum gauze, which is fitted with short wires that are connected by twisting to the leading-in wires proceeding from the aluminium rod. This electrode, which can be easily constructed in the laboratory, is very resistant to fracture owing to its resilience, and can, if necessary, be readily repaired. The weight of platinum

on the electrode *A* is about 7 grms., that on the electrodes *B* and *C* about 3 or 4 grms.

The electrode *D* is intended for use as an anode when the electrolyte to be analysed must not come in contact with it, so that oxidation may be avoided. For this purpose it is designed to hold a parchment thimble diaphragm, which revolves with it and holds an auxiliary electrolyte, say, of dilute acid or a salt. The thimble, of 16 mm. diameter, is cut to the correct length and provided with two slots at the top, slipped over the electrode after soaking in water and fastened to the funnel-shaped portion by means of thread. Since a small amount of the ions to be estimated will always diffuse through the parchment, the electrode is so designed that the whole of the liquid contained in the anode chamber formed by it may be forced into the cathode chamber towards the end of a determination, and be displaced by fresh liquid. For this purpose the electrode is constructed of an inner tube, *a*, with aluminium rod and four platinum leading-in wires similar to that used in electrode *C*. To the bottom of this tube is fused a protrusion carrying four arms to which the outer tube *b*, with a funnel top, is sealed. The bottom of the electrode thus represents the appearance shown by *s*. The tube *a* has four beads *p*, of such a size as to keep the tube *b* in position and thus strengthen the electrode, whereas the tube *b* carries two rows of eight beads for holding the platinum jacket *j*, the construction being similar to that described for electrode *B*. The leading-in wires are taken through the bottom of the electrode and twisted to short wires welded to the platinum jacket. The cathode used with this anode must be open at the top, the gauze usually rising above the level of the electrolyte. It will be seen that when fresh electrolyte is poured into the funnel *f* towards the end of a determination, the original electrolyte is forced down the annular space between *a* and *b*, and finally pushed upwards and into the cathode chamber through the slits at the top of the parchment. This electrode has been found to give good results in the rapid separation of copper from sulphate solutions containing large amounts of iron salts. It is obvious that good results can only be obtained in such solutions if the formation of ferric salts, which would dissolve the copper, is inhibited.

THE STAND AND ELECTRICAL CONNECTIONS.—Fig. 1 is a photograph of a complete stand, being one of four which are permanently set up for use on the same base. Fig. 3 is a diagram of the electrical connections, the same letters being used in these

figures to represent corresponding parts. The figures are self-explanatory, but the following remarks may be made. The resistance *R* shown is of 2.7 ohms and 14 ampères carrying capacity, and is arranged so that by alteration of the switch *s*₂ it may be used either in series or in shunt with the electrolytic

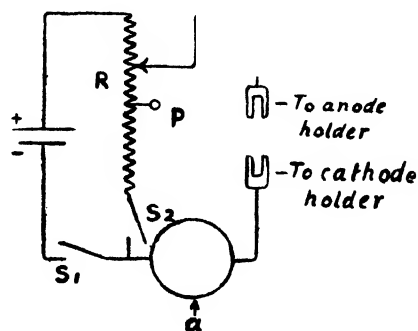


Fig 3

apparatus. Further, the latter is so arranged that by the interchange of two connections either the outer or the inner electrode may be made the cathode. The terminal *P* is fitted to allow the apparatus to be used for potentiometric

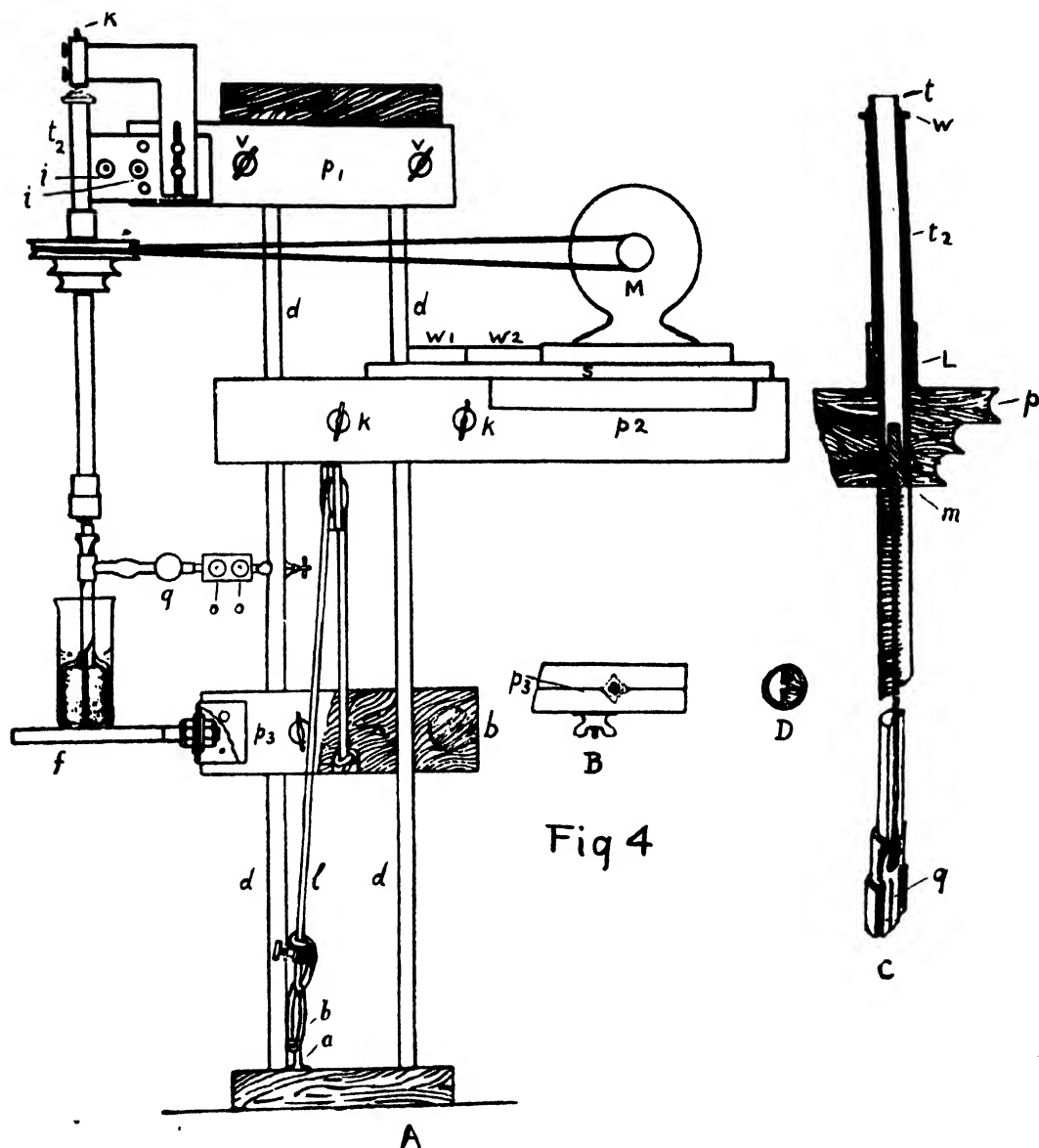


Fig 4

titrations according to the method of Roberts (*J. Amer. Chem. Soc.*, 1919, 41, 1358). A scale is fitted to the rheostat for convenience during potentiometric titrations.

Figs. 4A to 4D represent the central portion of the stand, giving details of

the stirring arrangement and the supports for beaker and electrodes. Two rods, d, d , of rustless steel, are fitted at each end to the wooden stand and serve as supports for the wooden crossbars, p_1, p_2, p_3 . Of these, p_1 and p_2 are screwed firmly to the rods, whereas p_3 slides readily on them, being provided with a hole of quadratic section which is lubricated with vaseline (see Fig. 4B). The motor is represented by M . It is controlled by the switch s_3 (Fig. 1), and a regulating resistance of 590 ohms and 0.7 amp. carrying capacity which is shunted across the 200 volt mains, the motor being connected with one end and the slider. The resistance is not visible in Fig. 1, being fitted to the back of the board holding the motor switch s_3 . The position of the motor and hence the tension on the pulley is controlled by two wedges, w_1, w_2 , or else by screws. The clutch holding the inner revolving electrode and the connection with it are shown in detail in Fig. 4C. A steel tube t_1 is suspended by means of a washer w inside a brass tube t_2 , which acts as a bearing to it. The steel tube also holds the oil trap l and the pulley p . It is closed at the bottom by a steel plug, m , of the shape shown, which is screwed and cemented into it. Electrical connection between m and the stationary terminals i, i (Fig. 4A) is made by means of mercury on which a drop of oil floats, and the steel wire k . The further flexible connection to the inner electrode is constructed of a strand of flexible copper wire, let into the plug m , and a rubber tube of 3/32 in. bore. The clutch is novel and requires detailed description. A segment of the rubber tube is removed by a razor at the bottom. It has a section of the relative size apparent from the blank portion shown in the cross section in Fig. 4D, and a length in the direction of the tube, of about one inch. The piece of rubber thus removed is replaced by one of metal of similar shape, preferably of silver, which is soldered or otherwise fastened to the lower end of the strand of flexible wire. Over the bottom of the rubber tube and the metal segment a tightly fitting rubber tube jacket is pushed to a height of about two inches. This rubber tube is turned on itself at the bottom, or else another piece of its own diameter of about one inch length is pulled over it, in order to produce some pressure on the metal segment. The latter projects about one-sixteenth inch below the bottom and has a V-groove filed into it. The rubber tube is cut so that about seven-eighths of the original interior is left at the bottom, and this is lubricated with common chalk. It will be seen that the whole arrangement forms a very simple clutch for the inner electrode, which is connected or disconnected by pushing its stem into, or pulling it out of, the rubber tube.

The clamp q holds the outer electrode. As in previous designs, the V-shaped jaw offers a metallic contact and may, if desired, be coated with silver foil, cork being left on the opposite jaw. The clamp is provided with two terminals, o, o , for connection with the source of current and the potentiometer.

The ring f for holding the beaker is fastened to the sliding bar p_3 , which has already been referred to; b is a counterpoise of lead. This bar is controlled by the leather pulley cord l . The brass ring b engages in the dresser hook a , which is cut off short, so that b may be removed from it without raising the beaker. The length of the cord l is made adjustable by the slip-knot arrangement provided at the

bottom, the loop of the slip-knot being held in position, as shown, by a screw clip fastened to the cord.

THE AUXILIARY ELECTRODE VESSEL.—In the auxiliary electrode formerly used, connection with the liquid under examination was made through a film of

electrolyte held round the barrel of a closed tap. This introduces a considerable resistance of uncertain magnitude, and is sometimes objectionable. It has been recently criticised by T. B. Smith (*Trans. Faraday Soc.*, 1928, 24, 216), who describes a number of new designs. For some time past I have reverted to the form shown in Fig. 5A, which illustrates the vessel fitted up as a quinhydrone electrode. A novel feature claimed for this electrode is the manner in which it is held, a matter which is by no means of negligible interest. A hollow stem *s* is sealed to the bottom of

the vessel, and this is dropped through two holes provided in the prongs of the fork *f*, which is adjustably fitted to the stand. The electrode and its support are also visible in Fig. 1. Connection with a reservoir bottle placed on the top of the stand is made through a piece of thick-walled rubber tubing *via* the tap *t*.

SIR JOHN CASS TECHNICAL INSTITUTE, E.C.3.

A New Test for Boric Acid and Borates.

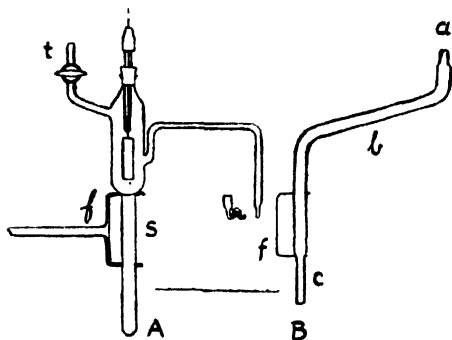
By A. SCOTT DODD, B.Sc., F.I.C., F.R.S.E.

(Read at the Meeting, February 6, 1929.)

VARIOUS methods have been suggested for the detection of boric acid. Of these, the best known is the turmeric test with its modifications. Probably the most delicate test is that with tincture of mimosa flowers (L. Robin, *ANALYST*, 1904, 29, 330), while for larger quantities the presence of boric acid is indicated by a green flame produced on igniting the substance with methyl alcohol or ethyl alcohol and glycerin.

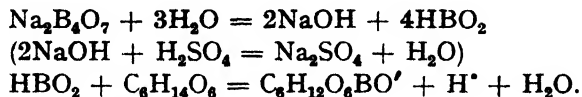
In a previous publication (*ANALYST*, 1929, 19) the author mentioned the pink coloration produced by the addition of mannitol and Sofnol Indicator No. 1 as characteristic of boric acid. Since then further investigations have been carried out to ascertain the soundness of the test, and to determine how it might be adapted for wider application.

Fig 5



As a test for borates in mixtures containing salts of various metals and borates, it was found to work very satisfactorily. Phosphates, arsenates, chromates, and tungstates appeared to be the only substances, which caused any interference with the distinctness of the reaction. The details of the test are as follows:

Place about 10 c.c. of the unknown substance in acid aqueous solution in a test tube. Add several drops of a solution of methyl red or Sofnol Indicator No. 1 and neutralise with caustic soda solution. Boil and filter into another test tube, if necessary; cool, add a drop or two of dilute sulphuric acid until the liquid is distinctly acid, and neutralise by dropping in 0.1 *N* sodium hydroxide solution until the pink colour just disappears. Add about 0.5 gm. of mannitol and shake the mixture. A distinct reddish-pink coloration is given if borates are present. The reaction is probably as expressed by the following equations:



The mannitol and boric acid complex is much more highly ionised than metaboric acid, and renders the solution distinctly acid and gives the characteristic reddish colour with the indicator employed.

It was found that the presence of small quantities of carbonic acid did not cause any appreciable interference with the test if 0.01 gm. of boric acid was present. It has been stated in some text-books that the reaction given with turmeric paper requires to be considered with caution, as "acid solutions of zirconic, titanitic, tantalitic, niobic and molybdic acids also colour turmeric paper brown," and may therefore be mistaken for boric acid. These acids, however, are not usually likely to be found. The author made careful comparisons of the reactions of two of the most common, namely, titanitic and molybdic acids, with those of boric acid.

It was found that, when using turmeric either in solution or on paper, confusion is likely to arise only when the quantity of these acids is large. With small quantities of the acids the stain on turmeric paper is merely brown in the case of molybdic acid, and dull reddish brown in the case of titanitic acid, whilst the stain given by boric acid is a bright rose pink. Further, when these stains are touched with a solution of caustic soda, the boric acid stain only is turned green.

The mannitol and Sofnol No. 1 test was also tried with molybdic acid and titanitic acid in the following manner:

A solution containing about 0.015 gm. of molybdic acid (MoO_3) and nitric acid was placed in a titrating basin, together with 2 drops of a solution of Sofnol Indicator No. 1, and neutralised with 0.1 *N* NaOH. When 0.5 gm. of mannitol was added no pink coloration was given, but when 3 c.c. 0.1 *N* boric acid solution, or 0.0186 gm. of boric acid was added, the solution became very distinctly bright pink. This solution was then titrated after addition of phenolphthalein, and was found to require 3.00 c.c. of 0.1 *N* sodium hydroxide solution, thus showing

that the presence of molybdic acid does not interfere with either the reaction or the determination of boric acid.

A similar test was tried with titanous chloride. As, however, this removed the colour from the Sofnol Indicator No. 1, even when acid was present, the following treatment was employed. A solution containing about 0.015 grm. of titanous chloride was placed in a titrating basin, and excess of caustic soda solution run in until a precipitate was formed. Then *N* sulphuric acid was added, drop by drop, until the solution was slightly, but distinctly, acid to litmus paper. The solution was boiled for 5 minutes, cooled and neutralised, two drops of Sofnol Indicator No. 1 being used. The results obtained were exactly similar to those given with molybdic acid, and showed also that the presence of titanous acid does not interfere with either the reaction or the determination of boric acid.

Solutions of titanous chloride and molybdic acid were also found to give negative reactions with mannitol and methyl red solution. Therefore, when dealing with mixtures containing large quantities of salts the mannitol and methyl red test appears to be at least as characteristic of boric acid as the turmeric test, and in some instances less liable to lead to erroneous conclusions.

The following substances were tested and were found to give negative results with the mannitol and methyl red test, and also did not interfere with the boric acid reaction when present along with borates:

Metallic Radicals.—Aluminium, ammonium, antimony, barium, bismuth, cadmium, calcium, cobalt, copper, iron, lead, lithium, magnesium, manganese, mercury, molybdenum, nickel, potassium, silver, sodium, strontium, tin, titanium, and zinc.

Acid Radicals.—Acetates, benzoates, bromates, bromides, chlorates, chlorides, citrates, formates, iodates, iodides, lactates, molybdates, nitrates, nitrites, oxalates, salicylates, sulphates, sulphides, sulphites, tartrates, and tannates.

In the case of arsenates, phosphates, chromates, and tungstates difficulty was experienced in ascertaining the exact point of neutrality, as the change in colour from red to yellow was not at all sharp. Tungstates differed from all the other substances examined, and gave a distinct reddish pink colour similar to that given by boric acid. This shows that tungstic acid resembles boric acid in that it also forms a complex with mannitol. The reaction, however, is much slower than in the case of boric acid and mannitol, the reddish pink colour reaching its maximum depth only after being allowed to stand for several minutes.

SENSITIVENESS OF THE MANNITOL AND METHYL RED TEST.—The sensitiveness of this test is not quite so great as that with turmeric paper. The latter is stated (Treadwell and Hall, Vol. I, p. 359) to give a visible reaction with 0.002 mgrm. of B_2O_3 , whereas this test was found to give a distinctly visible reaction with 0.2 mgrm., and a very distinct reaction with 0.3 mgrm. of boric acid (H_3BO_3) in 10 c.c.

The sensitiveness is increased by concentration, and 0.004 mgrm. of boric acid in 2 drops of liquid was found to give a visible reaction.

Glycerin or invert sugar may be used in place of mannitol, but the reaction is not quite so distinct with small quantities of boric acid. Glycerin was found to give a visible reaction with 0.3 mgrm. of boric acid in 10 c.c. of solution.

LABORATORY OF CITY ANALYST,
EDINBURGH.

DISCUSSION.

The PRESIDENT said that this contribution arose out of another paper, recently read, which gave rise to much discussion. Unfortunately, the interfering substance was phosphate, which was generally present when one was troubled with boric acid.

Dr. B. S. EVANS said that he would like to suggest as the method of neutralisation of the liquid in the case of phosphates the method which he always used, namely, the iodide and iodate method, which did not depend on any colour reaction at all, and which he had always found to be satisfactory. He would like to know whether Mr. Dodd's method had ever been applied to the detection of tungsten.

Dr. Cox, in the absence of the author, said that the reaction was certainly more sensitive than the ordinary test. Even in the presence of phosphates the colour was characteristic. He could not, of course, answer Dr. Evans's question with regard to tungsten.

Official Appointments.

THE Minister of Health has confirmed the following appointments:—

Dr. H. E. COX, M.Sc., F.I.C., as Public Analyst for the County of Cornwall (March 12th, 1929).

Mr. STANLEY DIXON, M.Sc., F.I.C., as Public Analyst for the County Borough of Cardiff (April 10th, 1929).

Mr. S. E. MELLING, F.I.C., as Public Analyst for the Borough of Accrington (formerly Joint Public Analyst) (April 16th, 1929).

Mr. J. H. SUGDEN, M.Sc., F.I.C., as Additional Public Analyst for the County Borough of Cardiff (April 19th, 1929).

Mr. A. LERRIGO, B.Sc., F.I.C., as Acting Public Analyst for the City of Birmingham (April 21st, 1929).

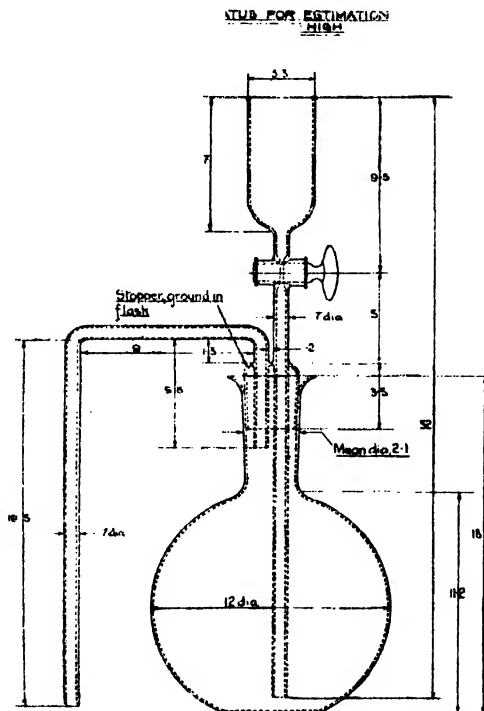
Mr. H. H. BAGNALL, B.Sc., F.I.C., as Public Analyst for the City of Birmingham (to date from July 1st, 1929).

Notes.

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

A RAPID METHOD FOR DISSOLVING HIGH CHROMIUM STEELS FOR THE DETERMINATION OF SULPHUR.*

IN the usual method for the gravimetric determination of sulphur in steel the sample is dissolved in *aqua regia*, which converts the sulphides present into sulphates; solution of an ordinary carbon steel is prompt, not to say violent. In the case of a high chromium steel, however, more especially of a stainless steel, the attack is very much less vigorous, and even when the metallic particles have



disappeared there usually remains a black sludge, presumably chromium carbide, on the bottom of the beaker, which often takes many hours' digestion on the hot plate to dispel it completely. The trouble appears to be bound up with the passivity induced by nitric acid, and the apparatus shown in the accompanying figure was devised in order to permit of the sample being dissolved first in hydrochloric acid alone, and afterwards oxidised with nitric acid.

* Communication from the Research Department, Woolwich.

The apparatus consists of a flask (cap. 700 c.c.) with a ground-in hollow stopper carrying a tapped funnel, the stem of which passes down to the bottom of the flask, and a leading tube whose short arm ends just below the stopper and whose long arm ends just above the level of the bottom of the flask.

PROCESS.—Five grms. of the sample are weighed into the flask, the stopper is inserted, and 25 c.c. of water are run in through the tapped funnel. The outer end of the leading tube is placed dipping to the bottom of a cylinder containing 35 c.c. of concentrated nitric acid, and 25 c.c. of concentrated hydrochloric acid are run into the flask cautiously through the funnel, the tap being then closed. The apparatus is allowed to stand until the evolution of gas slackens somewhat, after which it is placed on a double asbestos pad on the plate, the end of the delivery tube being kept dipped to the bottom of the cylinder containing the nitric acid the whole time. When the evolution of gas, which is at first increased, finally becomes quite slow, owing to the sample being nearly all dissolved, the tap of the funnel is opened to obviate the danger of the nitric acid being sucked back owing to accidental cooling by draughts. When evolution of gas has entirely ceased, the apparatus is removed from the plate, the tap being left open and the cylinder in position, and allowed to cool completely; when quite cold the tap is closed, and the top of the flask is held under a stream of hot water for a few seconds, care being taken that the sudden expansion of the air does not fling any drops of nitric acid out of the cylinder. The flask is then immediately held under the cold tap, so that the sudden contraction of the air shall draw all the nitric acid back into the flask; the points to be aimed at are:—

- (a) As far as possible, heating only the air in the flask and not the liquid.
- (b) Drawing the nitric acid back so quickly that it has not time to react with the ferrous salts before the cylinder is empty.

A violent reaction due to the oxidation of the ferrous salts and the carbon compounds, ensues; when this is over the cylinder and leading tube are rinsed into the flask by running about 20 c.c. of water into the former and allowing it to suck back in the same way as was done for the nitric acid, this operation being repeated two or three times. Finally, the contents of the flask are poured into a beaker and the flask, funnel and stopper thoroughly rinsed in; 5 c.c. of 20 per cent. potassium nitrate solution are added, the solution evaporated to dryness, and the sulphur determined in the ordinary way.

The following results were obtained with Messrs. Ridsdale's British Chemical Standard Steels:

Standard.	Mean result on certificate.	Result obtained.
N.	0.034	0.034
O.1	0.032	0.031
R.	0.052	0.049
A.2.	0.020	0.020
H.	0.047	0.043
W.	0.075	0.071

B. S. EVANS.

Legal Notes.

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

NON-ALCOHOLIC PRODUCTS SOLD AS GINGER BRANDY, AND ORANGE AND QUININE WINE.

ON March 6, a firm was summoned at Old Street Police Court, London, for selling ginger brandy which contained no brandy, and for selling orange and quinine wine deficient in quinine to the extent of 95 per cent.

Mr. W. G. Jenkins, prosecuting, said that the proceedings were taken under Sec. 2 of the new Food and Drugs (Adulteration) Act, 1928. The inspector had taken samples from men who were selling bottles of the preparations from door to door in Old Ford Road. On analysis the ginger brandy was found to contain no alcohol.

The solicitor for the defence said that the firm manufactured non-alcoholic wines, and that everyone in the district knew that alcoholic wines could not be sold without a licence. The label on the bottle was "Ginger Brandy (flavour), superior Non-Alcoholic." It was perfectly clear that it was not intended to have any brandy in it, and it was well known that 1s. 9d. (the price paid) was not the price of real ginger brandy.

With respect to the second summons, evidence was given that this was labelled "Orange Quinine Wine," and was being sold at 1s. 9d. per bottle.

Dr. F. L. Keith, Medical Officer for Bethnal Green, said that there was only a trace of quinine in the bottle. In cross-examination he agreed that there was an orange wine and a quinine wine in the British Pharmacopoeia, but not an orange and quinine wine.

Mr. A. E. Parkes, Public Analyst for Bethnal Green, gave evidence to the effect that the sample analysed by him was a solution of sugar containing a mere trace of quinine, and was devoid of alcohol.

For the defence it was stated that the article was sold as a beverage rather than as a medicine. The amount of quinine was not equivalent to that required by the British Pharmacopoeia, but they were now using a greater proportion of quinine.

The Magistrate (Mr. Snell) dismissed the first summons. With regard to the second summons, he said that it was clear that in that particular bottle there was not anything like the quantity of quinine a person might expect to get. He therefore inflicted a penalty of £5 with £2 10s. costs, and on the first summons the Borough Council would have to pay £2 10s. costs.

LABELLING OF BUTTER CREAM SANDWICHES.

A GROCER was summoned on March 14, at Lodon, Norfolk, for selling, to the prejudice of the purchaser, butter cream sandwiches not of the nature, substance, and quality demanded. On analysis, the sandwiches were found to contain "foreign fat, other than butter fat, to the extent of 100 per cent."

The defendant relied upon a warranty from a London firm, whose explanation was that what they meant to imply by the label was that the sandwiches had a butter flavour. The firm now recognised that the label was apt to mislead the public, and gave an undertaking to revise the description of these particular goods.

In these circumstances the Bench decided to dismiss the case against the defendant under the Probation of Offenders Act, on payment of £3 19s. costs.

New Zealand.

SIXTY-FIRST ANNUAL REPORT OF THE DOMINION LABORATORY.

IN his Report for the year 1927 the Dominion Analyst (Dr. J. S. Maclaurin) states that the total number of samples examined was 5086, of which 3420 were for the Public Health Department, 334 for the Customs, 666 for the Mines Department, and 24 for the Police. In addition, 2330 samples were analysed at the Auckland Branch Laboratory, and 2058 at the Christchurch Branch Laboratory.

MILK.—The number of samples taken in Wellington was 1708. Of these, 6 were watered, 8 had been skimmed, 2 were decidedly stale, and 15 were deficient in various ways. The use of an ice-chest by the inspector when taking samples in the summer months has proved effective in checking the sale of stale milk.

The milk samples (1607) examined at the Auckland Laboratory showed a considerable reduction in the amount of added water, and the cleanliness of the milk showed definite improvement as the result of rigid inspection.

The number of samples examined at the Christchurch Laboratory (1324) was much more satisfactory than in the previous year, but in view of the fact that there are probably 500 to 600 milk vendors in the city, more samples should be taken, so as to ensure that every vendor's milk will be sampled at least four or five times a year. The percentage of samples adulterated was 9.6, as compared with 10.6 for 1926. At the present time the City Council is making efforts towards municipalising the city milk supply.

SALT IN BEER.—In the early part of the year several samples contained more than the permissible amount of salt (50 grains per gallon), but later none of them exceeded the standard. Proceedings were taken against one brewer as the result of analyses in the Auckland Laboratory.

LIME WATER.—More than a third of the 49 samples examined were deficient in strength, and one contained lead. Of the 38 samples examined at the Christchurch Laboratory, nearly half were seriously deficient in lime, and a few had been made up with dirty water. In one or two cases common salt had been added. Sixty-five samples were examined at the Dunedin Branch Laboratory, and only 36 complied with the B.P. requirements.

CHARRED NOTES.—A quantity of ashes from a fire were examined for the Police, for evidence of banknotes alleged to have been burnt, and by careful examination a large number of fragments of notes were obtained. By cautious calcination twenty of the largest fragments were identified as part of the Bank of New Zealand £1 note. In the course of the investigation it was found that a number of the double-sided notes on issue in New Zealand are fairly resistant to destruction.

TOXICOLOGICAL CASES.—In connection with the cases investigated at the Wellington Laboratory, specimens were found to contain aniline oil, cocaine and holocaine, morphine, strychnine, and veronal.

At the Auckland Laboratory strychnine in sufficient quantity to cause death was found in four cases. In one series of cases pyridine was also found in the stomach, indicating that the alkaloid had probably been dissolved in methylated spirits. In another case the strychnine had been placed in a bottle of beer by some person unknown, the bitter taste of the alkaloid being momentarily masked by the taste of the beer.

Federated Malay States.

ANNUAL REPORT OF THE INSTITUTE FOR MEDICAL RESEARCH FOR 1927.

THE total number of samples examined for the various Government Departments in the chemical laboratories was 13,555, as compared with 7756 in 1926. The increase was chiefly due to samples of chandu dross, waters, toddies and stained articles.

MILK.—Five hundred and eleven samples were analysed, of which 75 were unsatisfactory. Samples are submitted by officers of the Health Branch, and also by officers of Sanitary Boards, all samples having been taken under the provisions of the Sale of Food and Drugs Enactment, 1913. Judging by the results of the analyses in the laboratory at Kuala Lumpur, there has been a considerable improvement in the quality of the milk supply in the last seven years.

TODDY.—Owing to the increased supervision of toddy shops there was a large increase in the number of samples examined, *viz.* 849, as compared with 171 in 1926.

Under the present regulations it is an offence to sell toddy in which:—(a) The alcoholic strength exceeds 10 per cent. by volume; (b) the acidity exceeds 0·8 per cent. expressed as acetic acid. These regulations were adopted to prevent (a) the fortification of toddy with spirit; (b) the sale of very old toddy. A method of detecting the watering of toddy has now been devised, and 263 of the samples gave indications of this adulteration, although conforming to the regulations (a) and (b).

RADION ALFA.—A proprietary remedy for malaria sold under this name was analysed. It was found to consist of methylene blue and quinine, and to be radioactive. Similar pills devoid of radioactivity were prepared, and alternate cases of malaria admitted to the hospital were given two of the proprietary pills or two of the equivalent pills twice daily. The results indicated that the addition of the radio-active substance did not materially increase the therapeutic value.

VITAMIN B EXTRACT.—The preparation of this extract from rice polishings was continued throughout the year, 27,680 fluid ounces being issued, as compared with 8960 ounces in 1926. The increased demand was due to the loss of vegetables caused by the floods in December, 1926.

An extract of rice polishings is now prepared in Java, and the anti-beri-beri vitamin from this extract is adsorbed on acid clay obtained from cheribou. The expense of concentration is thus avoided, and the product is obtained as a powder, which is made into tabloids.

An attempt was made in the Kuala Lumpur laboratory to adsorb the vitamin on purified kaolin, but the resulting product was of little value. The experiments are to be continued with Japanese clay.

BERI-BERI AND RICE "TOXIN."—During the rains and floods practically all the rice stocks in two districts became sodden with water. Conditions should therefore have been suitable for the generation of rice "toxin," which of recent years has received attention as a possible factor in producing beri-beri. But an analysis of cases in one of the districts brought out the interesting facts that among the Chinese the maximum number of cases occurred during the month following the floods, whereas the maximum was not reached for the Malays and Tamils until the third and fourth months, respectively. This is to be attributed, not to national idiosyncrasy, but to the fact that the normal Chinese diet approaches more nearly to the starvation line for vitamin B.

Another observation tending to discredit the toxin theory was made during the Kelantan outbreak. Rice stocks on a rubber estate were sodden with water for several days, but immediately after the floods subsided supplies of vegetables were obtained from outside and retailed to the coolies at nominal charges. No cases of beri-beri occurred on the estate. On a second estate rice stocks were kept quite dry throughout the flood period, but the vegetable gardens were washed out, and no attempt was made to obtain supplies. Cases of beri-beri developed among the coolies.

VIABILITY OF *Bacillus Typhosus* AND *V. Cholerae*.—The viability of intestinal pathogenic bacteria in river water is of local importance, because many natives deposit excrement directly into the river, and effluents from septic tanks discharge into drains leading to a river.

Samples were therefore obtained from the three streams (I, II and III) entering Kuala Lumpur and from the outgoing river (IV). In each flask 250 c.c. of river water were placed and infected with heavy doses of 1000 millions of *B. typhosus* or 3000 millions of *V. Cholerae*. Sub-cultures were made every 12 hours. *B. typhosus* was recovered for 3 days from specimens I, II and III, and for 4 days from specimen IV. The cholera vibrio was recovered for 2 days from specimen IV, and for 3 days from specimens I, II and III. Although it is not claimed that natural river conditions were closely simulated in the experiment, these results probably indicate the serious menace to the public health caused by the pollution of rivers.

Meteorological Office, Air Ministry.

CHANGES OF ZERO IN SPIRIT THERMOMETERS.*

IN an attempt to explain the fall of reading noted over a period of some years in the case of certain spirit thermometers, experiments have been carried out to ascertain the effect of the presence of acetone, in the filling liquid, upon the readings of spirit thermometers over a period of time. It is found that in the case of spirit thermometers containing acetone a marked fall of reading is obtained in course of time when the thermometers are exposed to light. It is suggested that the effect is due to the contraction of the liquid consequent upon the formation of condensation products from the acetone under the influence of light.

* Professional Notes, No. 51. By W. F. Higgins, M.Sc., and G. G. Bilham, B.Sc., A.R.C.Sc. H.M. Stationery Office, 1929. Price 4d. net.

The following conclusions have been drawn from the experiments described:

(1) In selecting a liquid for filling spirit thermometers, the presence of acetone as an impurity in the spirit should be carefully guarded against. A guarantee of freedom from acetone should be demanded from the firm supplying the spirit. (2) Owing to the common presence of acetone as an impurity in methylated spirit obtained from the usual sources, the use of this material, either in its commercial form or when redistilled, should be avoided. (3) Thermometers filled with either pure methyl or ethyl alcohol are stable over long periods. (4) The use of a mixture of ethyl and methyl alcohol should be avoided. (5) The addition of aniline colouring matter to pure ethyl alcohol does not affect the stability of the zero. (6) The nature of the residual gas, whether air or nitrogen, does not appear to affect the subsequent behaviour of the instrument. (7) The depression of zero associated with the presence of acetone occurs only on exposure to light.

An Appendix contains a note by the Government Chemist on the methods used for purifying the ethyl and methyl alcohols and the acetone used in these experiments, together with the tests of purity applied.

The International Temperature Scale.*

IN 1911 the directors of the national laboratories of Germany, Great Britain and the United States agreed to undertake the unification of the temperature scales used in their respective countries. This course was approved by the Fifth General Conference of Weights and Measures (1913), and at the Sixth General Conference (1921), it was decided to expand the field of activities of the International Committee and International Bureau, and to co-ordinate results obtained in other institutions. Finally, in 1927, the Seventh General Conference, representing 31 nations, adopted unanimously a resolution approving of the provisional adoption of an international scale, submitted for discussion by the Bureau of Standards, the National Physical Laboratory and the Physikalisch-Technische Reichsanstalt.

The English text of the Introduction and Definition of the Scale is as follows:

INTRODUCTION.—The experience of the Bureau of Standards, as of the National Physical Laboratory and of the Reichsanstalt, has for many years past indicated the necessity, for industrial purposes, of international agreement on a scale of temperatures ranging from that of liquid oxygen to that of luminous incandescent bodies. As a result of discussion extending over a considerable period, agreement has been reached by the three laboratories, subject to possible minor drafting amendments, on the attached specification for a practical scale, as affording a satisfactory basis on which uniformity in certification of temperature measurements for industrial purposes may be maintained.

It is to be understood that this proposal does not purport to replace the absolute temperature scale which it is recommended should be adopted, on principle, by the International Conference on Weights and Measures. It is intended merely to represent this scale in a practical manner with sufficient accuracy to serve the everyday needs of the laboratories for the purpose of industrial certifications, and is to be regarded as susceptible of revision and amendment as improved and more accurate methods of measurement are evolved.

It is anticipated that this scale will shortly be adopted by the three laboratories for the purposes indicated, and the attached draft is presented to the conference for consideration, with the recommendation that it should be officially adopted, with such amendments, if any, as may be agreed on, as the best practical realisation at the present time of the ideal thermometric scale.

* Report of the National Physical Laboratory for the Year 1928, pp. 29—33.

PART I. DEFINITION OF THE INTERNATIONAL TEMPERATURE SCALE.

1. The Thermodynamic Centigrade Scale, on which the temperature of melting ice, and the temperature of condensing water vapour, both under the pressure of one standard atmosphere, are numbered 0° and 100° , respectively, is recognised as the fundamental scale to which all temperature measurements should ultimately be referable.

2. The experimental difficulties incident to the practical realisation of the thermodynamic scale have made it expedient to adopt for international use a practical scale designated as the International Temperature Scale. This scale conforms with the thermodynamic scale as closely as is possible with present knowledge, and is designed to be definite, conveniently and accurately reproducible, and to provide means for uniquely determining any temperature within the range of the scale, thus promoting uniformity in numerical statements of temperature.

3. Temperatures on the international scale will ordinarily be designated as " $^{\circ}\text{C.}$," but may be designated as " $^{\circ}\text{C. (Int.)}$ " if it is desired to emphasise the fact that this scale is being used.

4. The International Temperature Scale is based upon a number of fixed and reproducible equilibrium temperatures to which numerical values are assigned, and upon the indications of interpolation instruments calibrated according to a specified procedure at the fixed temperatures.

5. The basic fixed points and the numerical values assigned to them for the pressure of one standard atmosphere are given in the following table, together with formulae which represent the temperature (t_p) as a function of vapour pressure (p) over the range 680 to 780 mm. of mercury.

6. Basic fixed points of the International Temperature Scale—

(a) Temperature of equilibrium between liquid and gaseous oxygen at the pressure of one standard atmosphere (oxygen point)	$^{\circ}\text{C.}$ - 182.97
$t_p = t_{760} + 0.0126(p - 760) - 0.0000065(p - 760)^2$	
(b) Temperature of equilibrium between ice and air-saturated water at normal atmospheric pressure (ice point)	0.000
(c) Temperature of equilibrium between liquid water and its vapour at the pressure of one standard atmosphere (steam point)	100.000
$t_p = t_{760} + 0.0387(p - 760) - 0.000023(p - 760)^2$	
(d) Temperature of equilibrium between liquid sulphur and its vapour at the pressure of one standard atmosphere (sulphur point)	444.60
$t_p = t_{760} + 0.0909(p - 760) - 0.000048(p - 760)^2$	
(e) Temperature of equilibrium between solid silver and liquid silver at normal atmospheric pressure (silver point)	960.5
(f) Temperature of equilibrium between solid gold and liquid gold at normal atmospheric pressure (gold point)	1,063

Standard atmospheric pressure is defined as the pressure due to a column of mercury 760 mm. high, having a mass of 13.5951 g/cm³, subject to a gravitational acceleration of 980.665 cm/sec.², and is equal to 1,013,250 dynes/cm².

It is an essential feature of a practical scale of temperature that definite numerical values shall be assigned to such fixed points as are chosen. It should be noted, however, that the last decimal place given for each of the values in the table is significant only as regards the degree of reproducibility of that fixed point on the International Temperature Scale. It is not to be understood that the values are necessarily known on the Thermodynamic Centigrade Scale to the corresponding degree of accuracy.

7. The means available for interpolation lead to a division of the scale into four parts.

(a) From the ice point to 660°C. the temperature t is deduced from the resistance R_t of a standard platinum resistance thermometer by means of the formula

$$R_t = R_0 (1 + A + Bt^3).$$

The constants R_0 , A , and B of this formula are to be determined by calibration at the ice, steam, and sulphur points, respectively.

The purity and physical condition of the platinum of which the thermometer is made should be such that the ratio R_t/R_0 shall not be less than 1.390 for $t=100^\circ$ and 2.645 for $t=444.6^\circ$.

(b) From -190° to the ice point, the temperature t is deduced from the resistance R_t of a standard platinum resistance thermometer by means of the formula,

$$R_t = R_0 [1 + At + Bt^2 + C(t-100)t^3].$$

The constants R_0 , A , and B are to be determined as specified above, and the additional constant C is determined by calibration at the oxygen point.

The standard thermometer for use below 0° C. must, in addition, have a ratio R_t/R_0 less than 0.250 for $t = -183^\circ$.

(c) From 660° C. to the gold point, the temperature t is deduced from the electromotive force e of a standard platinum *v.* platinum-rhodium thermo-couple, one junction of which is kept at a constant temperature of 0° C., while the other is at the temperature t defined by the formula

$$e = a + bt + ct^2.$$

The constants a , b , and c are to be determined by calibration at the freezing point of antimony, and at the silver and gold points.

(d) Above the gold point the temperature t is determined by means of the ratio of the intensity J_2 of monochromatic visible radiation of wave length λ cm., emitted by a black body at the temperature t_2 , to the intensity J_1 of radiation of the same wave length emitted by a black body at the gold point, by means of the formula

$$\log_e \frac{J_2}{J_1} = \frac{c_2}{\lambda} \left[\frac{1}{1.336} = \frac{1}{(t+273)} \right]$$

The constant c_2 is taken as 1.432 cm. degrees. The equation is valid if $\lambda(t+273)$ is less than 0.3 cm. degrees.

Part II deals with the recommended experimental procedure for determining: (1) The temperature of equilibrium of liquid and gaseous oxygen; (2) the temperature of melting ice; (3) the temperature of condensing water vapour; (4) the temperature of condensing sulphur vapour; (5), (6) and (7) for standardising a thermo-couple; (8) subsidiary points.

Revised Table of Atomic Weights for 1929.

THE Council of the Chemical Society has ordered the following table to be published in their journal (*J. Chem. Soc.*, 1929, 216). In the accompanying Report, which is signed by Messrs. F. W. Aston, H. V. A. Briscoe, R. Whytlaw Gray, and E. K. Rideal, it is stated that Clarke's method of computation being considered trustworthy, his final values for the 36 elements for which no determinations have since been published have been adopted. In other cases Clarke's figures have been modified in accordance with more recent work.

For the nine "simple" elements, H, He, C, N, F, Na, P, As, and I, the values obtained by Aston, with his new mass-spectrograph, are adopted in preference to those obtained from "physical" or "chemical" data, as the Committee are of opinion that Aston's is less liable to error than any other method.

Where definite information is available the mass-numbers of the known isotopes of the elements are also given, in the order of their abundance, as deduced from the relative intensities of the lines in the mass-spectrum. In cases where the last figure may be in error by two or three units it is given as a subscript.

ATOMIC WEIGHTS. 1929.

Atomic number.	Name.	Symbol.	Atomic weight.	Mass-numbers of isotopes in order of intensity.
1	Hydrogen	H	1.0078	1
2	Helium	He	4.002 ₁	4
3	Lithium	Li	6.94	7, 6
4	Beryllium	Be	9.02	9
5	Boron	B	10.83	11, 10
6	Carbon	C	12.003 ₆	12
7	Nitrogen	N	14.008	14
8	Oxygen	O	16.0000	16
9	Fluorine	F	19.00	19
10	Neon	Ne	20.18	20, 22, 21
11	Sodium	Na	23.000	23
12	Magnesium	Mg	24.30	24, 25, 26
13	Aluminium	Al	26.97 ₀	27
14	Silicon	Si	28.0 ₈	28, 29, 30
15	Phosphorus	P	30.98 ₂	31
16	Sulphur	S	32.06 ₅	32, 33, 34
17	Chlorine	Cl	35.457	35, 37
18	Argon	A	39.94	40, 36
19	Potassium	K	39.10 ₅	39, 41
20	Calcium	Ca	40.09	40, 44
21	Scandium	Sc	45.1 ₁	45
22	Titanium	Ti	47.90	48
23	Vanadium	V	50.95	51
24	Chromium	Cr	52.04	52
25	Manganese	Mn	54.95	55
26	Iron	Fe	55.84	56, 54
27	Cobalt	Co	58.95	59
28	Nickel	Ni	58.69	58, 60
29	Copper	Cu	63.55	63, 65
30	Zinc	Zn	65.38	64, 66, 68, 67, 65, 70, 69
31	Gallium	Ga	69.72	69, 71
32	Germanium	Ge	72.60	74, 72, 70, 73, 75, 76, 71, 77
33	Arsenic	As	74.93 ₁	75
34	Selenium	Se	79.2	80, 78, 76, 82, 77, 74
35	Bromine	Br	79.91 ₅	79, 81
36	Krypton	Kr	82.9	84, 86, 82, 83, 80, 78
37	Rubidium	Rb	85.4 ₂	85, 87
38	Strontium	Sr	87.6 ₂	88, 86
39	Yttrium	Yt	88.9 ₂	89
40	Zirconium	Zr	91.2	90, 94, 92, (96)
41	Niobium	Nb	93.3	
	(Columbium)	(Cb)		
42	Molybdenum	Mo	96.0	
43	Masurium	Ma	—	
44	Ruthenium	Ru	101.6 ₅	
45	Rhodium	Rh	102.9	
46	Palladium	Pd	106.7	
47	Silver	Ag	107.880	107, 109
48	Cadmium	Cd	112.4 ₀	114, 112, 110, 113, 111, 116
49	Indium	In	114.8	115
50	Tin	Sn	118.70	120, 118, 116, 124, 119, 117, 122, 121, 112, 114, 115
51	Antimony	Sb	121.76	121, 123
52	Tellurium	Te	127.5	128, 130, 126
53	Iodine	I	126.93 ₂	127
54	Xenon	Xe	130.2	129, 132, 131, 134, 136, 128, 130, 126, 124
55	Caesium	Cs	132.8 ₁	133
56	Barium	Ba	137.3 ₆	138
57	Lanthanum	La	138.9 ₀	139
58	Cerium	Ce	140.2	140, 142

Atomic number.	Name.	Symbol.	Atomic weight.	Mass-numbers of isotopes in order of intensity.
59	Praseodymium	Pr	140.9	141
60	Neodymium	Nd	144.2 ₆	142, 144, 146, (145)
61	Illinium	Il	—	
62	Samarium	Sm	150.4 ₆	
63	Europium	Eu	152.0	
64	Gadolinium	Gd	157.0	
65	Terbium	Tb	159.2	
66	Dysprosium	Dy	162.4 ₆	
67	Holmium	Ho	163.5	
68	Erbium	Er	167.6	
69	Thulium	Tm	169.4	
70	Ytterbium	Yb	173.0	
71	Lutecium	Lu	175.0	
72	Hafnium	Hf	178.6	
73	Tantalum	Ta	181.3	
74	Tungsten	W	184.1	
75	Rhenium	Re	—	
76	Osmium	Os	191.0	
77	Iridium	Ir	193.0 ₄	
78	Platinum	Pt	195.2	
79	Gold	Au	197.2 ₁	
80	Mercury	Hg	200.6 ₀	202, 200, 199, 198, 201, 204, 196
81	Thallium	Tl	204.3	
82	Lead	Pb	207.2 ₁	208, 206, 207
83	Bismuth	Bi	209.0 ₀	
84	Polonium	Po	—	
85	—	—	—	
86	Niton (Emanation)	Nt (Em)	222	
87	—	—	—	
88	Radium	Ra	225.9 ₆	
89	Actinium	Ac	—	
90	Thorium	Th	232.15	
91	Proto-actinium	Pa	—	
92	Uranium	U	238.1 ₆	

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Difference in Osmotic Concentration between Yolk and White of Egg.

J. Straub. (*Rec. Trav. Chim. Pays-Bas*, 1929, **48**, 49–82.)—The difference in osmotic concentration between yolk and white of hens' eggs, indicated by the respective freezing points, about -0.6° C. and -0.45° C., is discussed. Results are given of calculations of the partial freezing point depressions, due to the known proportions of the various soluble constituents of yolk and white, and the sum of these is about 0.52° C. for the former, and about 0.27° C. for the latter, the divergences from the actual figures being thus 0.08° and 0.18° respectively. Since the skin of the living yolk is permeable by water, equilibrium between yolk and white would indicate an over-pressure of 1.8 atmos. in the yolk, and the conclusion is drawn that such equilibrium does not exist in the resting eggs. The maintenance of a stationary state other than one of equilibrium demands a continuous supply of energy, and the possible sources of this are considered.

T. H. P.

Comparison of the Monier-Williams and the A.O.A.C. Methods for Determination of Sulphurous Acid in Food Products. J. Fitelson. (*J. Assoc. Off. Agric. Chem.*, 1929, 12, 120-129.)—A comparison of the Monier-Williams method for determining sulphurous acid (*ANALYST*, 1927, 52, 343, 415) with the A.O.A.C. method establishes the need of a more accurate method than that of the A.O.A.C. in the case of food products containing volatile sulphur compounds. The use of copper salts as a wash trap to remove sulphides from the distillate in the official method is shown to produce inaccuracies, and the accuracy and reliability of the Monier-Williams method under varied conditions is confirmed. In the course of a detailed study of brined onions it is conclusively shown that little or no sulphurous acid is developed during brining, so that where detected by the Monier-Williams method it is added, and that shown by the A.O.A.C. method can be taken as a rough indication of the quantities of volatile sulphur compounds present in the onions. The use of brine reduces the volatile sulphur, this being largely due to a leaching out by the brine. D. G. H.

Solubility Tests of Castor Oil. H. P. Trevithick and M. F. Lauro. (*Oil and Fat Ind.*, 1929, 6, 27-29.)—Failure of castor oils to pass solubility tests, especially where alcohol of less than 95 per cent. strength is used, is not to be considered proof of adulteration without a further chemical investigation. Castor oil thickens on keeping, gravity and viscosity increasing without change in iodine value. The acetyl value furnishes one of the most useful indicative figures, and it is considered that the filtration method in determining the acetic acid liberated from the acetylated oil should not be used, but that distillation of the saponified acetylated fat with phosphoric acid is more trustworthy. D. G. H.

Indian Ephedras. Their Extraction and Assay. S. Krishna and T. P. Ghose. (*J. Soc. Chem. Ind.*, 1929, 48, 67-70T.)—The content of ephedrine in the Chinese plants "Mahuang" (*Ephedra sinica* and *E. equisitina*) does not depend on the altitude at which the plants are grown, but diminishes as the rainfall of the locality increases. It is determined as follows: 100 grms. of the air-dried (about 5 per cent. of moisture) and finely-powdered green stems are treated for 2 hours with 400 c.c. of a mixture of 3 parts of ether and 1 part of chloroform, the mass being then well shaken with 50 c.c. of ammonia (3 parts of 0.880 ammonia and 1 part of water), left overnight and filtered. The residue is treated twice in the same way. The combined extracts are distilled to remove the bulk of the solvent, and the residue is extracted with 75, 60, 60, and 50 c.c. of 1.5 per cent. hydrochloric acid. The total acid extract is filtered, made strongly alkaline with potassium carbonate and almost saturated with salt, the alkaloids thus liberated being extracted four times with ether. The bulk of the ether is distilled off and the rest allowed to evaporate at room temperature. Excess of 0.1 *N* hydrochloric acid is added, and the excess titrated with 0.1 *N* sodium hydroxide in presence of methyl orange, the total amount of alkaloid being calculated as ephedrine. The titrated solutions are rendered alkaline, and the alkaloids again extracted with

ether and treated with alcoholic hydrochloric acid to convert them into the hydrochlorides, which are dried over calcium chloride and caustic potash in a vacuum desiccator. Finally, ephedrine hydrochloride is isolated from the mixed hydrochlorides by treatment with dry chloroform, in which it is practically insoluble: 100 c.c. of chloroform dissolve 0.02 gm. of ephedrine hydrochloride at 15°, 0.04 gm. at 30°, and 0.084 gm. at 60° C. The hydrochloride is dried and weighed. The large-scale extraction is also described.

T. H. P.

Biochemical.

Bio-assay of Commercial Pituitary Powders. W. T. McClosky and J. C. Munch. (*J. Assoc. Off. Agric. Chem.*, 1929, **12**, 135-136.)—Analyses of commercial samples of pituitarium (cleaned dried powdered posterior pituitary lobes of domesticated animals used for food) showed activities which were generally between 30 and 50 per cent. of the standard posterior pituitary powder, U.S.P.(X.); commercial anterior powders were uniformly inactive by the U.S.P. method on guinea-pig uterus, and commercial whole powders showed a ratio of activity of 1 part of posterior substance in 8 parts of whole body. It is suggested that the standards for physiological activity should be; for pituitarium U.S.P. 50 per cent., and for desiccated whole pituitary powder 5 per cent. of the activity of the U.S.P. official standard posterior pituitary powder.

D. G. H.

Comparison of the Oxytocic, Pressor and Anti-Diuretic Activities of Commercial Samples of Pituitary Extract. U. G. Bijlsma, J. H. Burn and J. H. Gaddum. (*Quart. J. Pharm.*, 1928, **1**, 493-508.)—The standardisation of pituitary extract is almost universally effected by comparison with the international standard on the isolated guinea-pig uterus. It has been suspected that this comparison is not always an accurate guide to the pressor potency of different extracts, and some clinical reports have indicated that it is not a guide to the anti-diuretic potency. The recent separation of oxytocin and vasopressin by Kamm, Aldrich, Grote, Rowe, and Bugbee (*J. Amer. Chem. Soc.*, 1928, **50**, 573) has furnished final proof that the oxytocic and pressor properties are due to two different substances, and possibly the anti-diuretic effect is due to a third. It was therefore thought important to determine how far differences in anti-diuretic and pressor potency arise in commercial extracts of approximately equal oxytocic power. Four commercial extracts of the posterior lobe of the pituitary have thus been examined in comparison with the international standard for their oxytocic and pressor power by the three authors working entirely independently, and three separate reports are presented. One worker has also tested their anti-diuretic power on the unanaesthetised dog; another has devised and described a new method of testing for this action on a normal human being. In the discussion the average values of the investigators are compared, and the following conclusions are drawn:—The results of the different workers agree with one another, except that there are differences of opinion as to both the pressor and oxytocic powers of one of the

extracts and as to the anti-diuretic power of another. The anti-diuretic effect is not due either to the pressor or to the oxytocic principle. The test for any one of these three active principles does not provide a reliable index of the concentration of any other of them in commercial extracts. The present international standard can only be used as a standard for anti-diuretic activity if it is found that different preparations of it contain the same concentration of the anti-diuretic principle ; if different samples are alike, the existing standard will serve as a standard for all three properties.

P. H. P.

Creatine Content of the Muscles and some other Tissues in Fishes.

A. Hunter. (*J. Biol. Chem.*, 1929, **81**, 513-523.)—The creatine content of the skeletal muscles has been determined in fifteen species of fishes from the coast of British Columbia. Each genus, with two exceptions, was represented by at least two individuals, some by as many as four. In several cases the heart or the testis or both were also analysed, and in two instances only (those of the dogfish and the skate) the brain was examined. It was not possible to obtain and examine each of the species under identical conditions, *e.g.*, some had been kept in a pen and others were captured in the open. Considerable differences were found to exist between different species, and also between different individuals of the same species, yet each species presents a fairly characteristic range of creatine values. The results obtained are tabulated. In the mammal different muscles often show differences of creatine content, and thus a comparison of species must be based upon analyses of homologous muscles or muscle groups. In order to test whether this applied to fishes, three samples of flesh were taken from each of two ling cod (*Ophiodon elongatus*), (1) from the dorsal region just behind the head, (2) from the abdominal wall, midway between the head and tail, and (3) from the compact mass of muscular tissue posterior to the cloacal aperture. There was found to be a progressive and conspicuous increase of creatine concentration from before backward, *i.e.* the highest value was in the powerful propelling muscles of the tail. Therefore in most other cases samples were taken only from the caudal region, but in the case of the skate, the laterally disposed muscles of the pectoral fins, used for propulsion were found to contain as much creatine as those of the tail. The differences between species do not correspond in any obvious way with zoological subdivisions ; there is no systematic difference, with respect to muscle creatine, between the Teleostomi and the Elasmobranchs. The highest figure found for tail muscle (0.74 per cent.) is in one of the Teleostomi (*Clupea*), the lowest (0.48) in a selachian (*Raia*) ; the ratfish (grouped as an elasmobranch), shows 0.55 per cent., and the dogfish, another Elasmobranch, 0.63 per cent. The elasmobranchs show a lower concentration of creatine in the heart than the Teleostomi. In general, the skeletal muscles of fish contain more creatine than those of mammals. Mammalian muscle exceeds 0.6 per cent. in a few isolated cases, the mixed flesh of the rabbit shows an average of 0.53, and the muscles of most other mammals yield less than 0.5 per cent. In seven out of the thirteen genera of fishes represented, the average concentration is close to 0.6 per cent., in three (*Hydrolagus*, *Sebastes* and *Leptocottus*),

it lies between 0.5 and 0.6; in one (*Phanerodon*) between 0.6 and 0.7. In one only (*Raia*), it falls below 0.5, and in *Clupea* it even exceeds 0.7. Mammals, however, show a higher concentration of creatine in the heart and in the testes. The two analyses made of selachian brain tissue indicate a content of creatine equal to that of mammalian brains. In fishes, as in mammals and birds, red muscles contain less creatine than pale, and foetal muscle less than the adult. It cannot safely be assumed that creatine exists in fish muscle in exactly the same state as in mammalian muscle.

P. H. P.

Colorimetric Determination of Total and Inorganic Sulphates in Blood Serum, Urine and other Body Fluids. E. G. Wakefield. (*J. Biol. Chem.*, 1929, **81**, 713-721).—A colorimetric method for the determination of sulphates, the principle of which was originally described by Hubbard (*J. Biol. Chem.*, 1927, **74**, 5), has been checked after certain changes which gave most consistent results had been made, and has been found to be a microchemical method which is adaptable for clinical uses. Hubbard's process was for the determination of inorganic sulphates in blood serum. The reagents described by him are retained, but certain portions of the manipulative procedure and the strengths of some of the solutions have been modified, and the method has been extended to permit the determination of total and conjugated sulphates in the blood serum, and of total, inorganic and conjugated sulphates in the urine and in the fluids which in oedematous conditions collect in the peritoneal cavity, thorax and elsewhere. The method consists in treatment of the serum or urine with trichloroacetic acid to remove the proteins, centrifuging, and addition of the supernatant fluid to a solution of benzidine base. The precipitate of benzidine sulphate is washed in acetone, centrifuged, drained, dissolved in dilute hydrochloric acid, and treated with diluted hydrogen peroxide and 0.5 per cent. ferric chloride solution. The yellow colour thus formed is fully developed after about 5 minutes, and remains constant until about 10 minutes have passed; a few drops of concentrated hydrochloric acid added to the standard and the unknown will prevent the rapid fading of the colours if readings cannot be made during the second five minutes. The acidity must be the same in the standards and the unknown. Normal values for the total, inorganic and conjugated sulphate content of the blood serum, as determined by this method, are given. This study confirms the results of Denis and Reed (*J. Biol. Chem.*, 1926, **71**, 191; *ANALYST*, 1927, **52**, 96), who demonstrated the presence of conjugated sulphates in human blood.

P. H. P.

Association of Vitamin A with Greenness in Plant Tissue. II. Vitamin A content of Asparagus. J. W. Crist and M. Dye. (*J. Biol. Chem.*, 1929, **81**, 525-532).—It has previously been shown by Dye, Medlock and Crist (*J. Biol. Chem.*, 1927, **74**, 95; *ANALYST*, 1927, **52**, 552) that the vitamin A content of head and leaf lettuce varies more or less directly with the greenness of the plant tissue. Since asparagus is offered for consumption in both the green and bleached state, and also as a canned product, an investigation has been made of its vitamin A content. Different types and varying amounts of asparagus were given to albino

rats, which had been placed on a vitamin *A*-free diet until their store of the vitamin was depleted, and growth was determined over a period of 8 weeks. Curves show the results. Green asparagus, whether fresh, freshly cooked, or canned, when given daily at the rate of 0.1 grm. per animal, contained vitamin *A* in sufficient quantities to promote health and growth in the rats. Fresh, bleached (term used where tissues have never been allowed to become green) asparagus, given daily at the rate of either 0.1 or 0.5 grm. per animal gave no stimulus to health and growth; the animals died as rapidly as the negative controls. Cooking in open kettle fashion effected an improvement in the nutritive quality of bleached asparagus, but did not render its value comparable to that of the green product cooked in the same manner. Green asparagus tissue had lower percentages of water and iron than the bleached tissue, but higher percentages of ash, nitrogen, sulphur, calcium, phosphorus, and possibly manganese. The quantities of manganese were so small that the figures could not be taken as significant. The data from these experiments support the conclusion that the vitamin *A* content of plant tissue is associated with its greenness. There is no direct evidence that the chlorophyll is the vitamin, but where the tissues are decidedly green the vitamin is abundant. It is an open question whether or not the chlorophyll or some part of the chlorophyll molecule, *e.g.*, the phytol alcohol unit, is the vitamin, or functions in the production of the vitamin, or is merely a circumstance attendant upon the reactions of the plant when the environment is such as to effect the synthesis of the vitamin. It is possible that the poor quality of bleached asparagus as food for the animal may not be due alone to vitamin *A* deficiency, but also to a superabundance of deleterious chemical compounds. P. H. P.

The Vitamin *A*, *B* and *C* content of Artificially Versus Naturally Ripened Tomatoes. M. C. House, P. M. Nelson and E. S. Haber. (*J. Biol. Chem.*, 1929, **81**, 495-504.)—The use of ethylene in the ripening of fruits and vegetables (used to a limited extent commercially during the past 3 years) possesses distinct advantages over the older method. However, since the consumer is interested in the nutritive constituents as well as in the exterior appearance of the final product, and fruits and vegetables are eaten largely because of their vitamin value, it is of interest to know the effect this new commercial method of ripening has upon the vitamin content. Therefore the vitamin content of tomatoes, a foodstuff commonly subjected to this treatment, was investigated. A comparison was made of the vitamin *A*, *B* and *C* content of green, air-ripened, ethylene-ripened and vine-ripened tomatoes. Twenty rats were used in each group for the vitamin *A* and *B* tests. Ten guinea pigs were used in each group for the vitamin *C* tests. Statistical treatment of the data has shown that:—The four lots of tomatoes showed no difference in their vitamin *B* content, and thus the methods of ripening used did not alter the amount of vitamin *B* present in the green mature fruit. The vitamin *A* content of ripened tomatoes was found to be greater than that of the green mature fruit. The same quantity of vitamin *A* was developed in the tomatoes regardless of the method of ripening used. The green tomatoes were

relatively poor in vitamin C. Air-ripened and ethylene-ripened tomatoes were richer in this vitamin than the green fruit, and vine-ripened tomatoes were superior to either the artificially ripened or the green tomatoes. Therefore the commercial method of ripening tomatoes in an ethylene-air mixture (1:800 was used) produces fruit which is equally as rich in the vitamins A, B and C as fruit which has been picked green and ripened in air.

P. H. P.

Variations in Amounts of the Antirachitic Vitamin in Different Samples of Cod-liver Oil, Milk and Butter. K. H. Coward. (*Quart. J. Pharm.*, 1928, 1, 534-538.)—A large number of substances have been examined for their content of vitamin D by the method described by Coward (*Quart. J. Pharm.*, 1928, 1, 27; *ANALYST*, 1928, 53, 449), in which the amount of activity contained in 0.0001 mgrm. of a standard preparation of irradiated ergosterol is adopted as a unit of antirachitic activity. It is shown that different samples of cod-liver oil, milk, and butter may vary enormously in their antirachitic potency, and the object of the paper is to call attention to these variations. Four selected samples of cod-liver oil were found to contain 150, 100, 70-80, and 50 units of antirachitic activity per grm., respectively. So great a variation amongst selected samples suggests a still greater variation in a series bought in the open market. Probably samples of spring and summer high-priced butters are approximately equal in their content of vitamin D (some showed 0.8 to 1.0 unit per grm.), but in some instances the butter could not be expressed in units, as there was no comparison with the standard (margarine containing a vitamin concentrate). One sample was extremely poor in the antirachitic factor. Two out of three samples of milk were almost entirely lacking in vitamin D. Since one of these two was examined in midsummer, it seems probable that all winter milk will be found deficient. It is evident that the widespread belief that milk and butter are rich sources of the antirachitic vitamin is largely erroneous. Recent evidence does not challenge the view that a sufficiency of the fat soluble vitamins (A and D) will always be obtained in a diet containing plenty of milk and butter, so far as vitamin A is concerned, but it may well be that it is often not true for vitamin D, and that, in order to ensure the presence of enough of the latter, it should be added specifically in one of the available forms. It is suggested that the advertisement of preparations containing added vitamin D as substitutes for cod-liver oil will be misleading unless the amount of vitamin present in the daily dose for a child is 150 units, or for an adult 300 units. Substitutes for cod-liver oil must also contain vitamin A. If other laboratories in Great Britain desire to state their results in terms of the same units, the Pharmacological Laboratory is prepared to supply a small portion of the standard sample of irradiated ergosterol on request.

P. H. P.

Photochemical Action of Various Sterols. L. Hugounenq and E. Couture. (*Comptes rend.*, 1929, 10, 742-743.)—Cholesterol from cod-liver oil gives, after 5 days, an impression on a sensitive plate through a quartz plate, but

loses its activity after a month in the dark. It appears to be a phenomenon of phosphorescence, and a sample kept for some months in diffuse light was more active than one freshly prepared. Sterols from cow's blood and from snails gave no impression after 15 days, but that from the silkworm gave a clear positive effect. Ergosterol from pure yeast gave a clear stain on sensitised gelatin either in direct contact or when separated by a layer of 3 mm. of air or a thin film of collophane. Samples from less pure yeasts under similar conditions showed more intense reactions.

D. G. H.

Agricultural.

Determination of Small Quantities of Nitrogen in Plant Materials.

J. T. Sullivan and L. E. Horat. (*J. Assoc. Off. Agric. Chem.*, 1929, 12, 133-135.)

—The nitrogen in plant-materials rich in organic matter but low in nitrogen may be determined with as high an accuracy as the Kjeldahl method gives with larger samples, by an application of the Folin and Farmer method. Plant extracts are treated in a Kjeldahl flask by boiling off the water or alcohol from the acidified extract and digesting with 1-2 grm. of copper sulphate and 3 c.c. of concentrated sulphuric acid. Superoxol may be added when fumes appear, or more sulphuric acid is used. Heating is continued for 1 hour after clearing of the solution, which, after cooling, is transferred to a test tube; washings are added followed by 5 c.c. of saturated sodium hydroxide, and, after again cooling, 10 c.c. of alkali completes neutralisation, and a 2 hours' aeration is carried out in the Van Slyke-Cullen urea apparatus with 0.02 *N* sulphuric acid. Methyl red is used in the back titration. The nitrogen in dry apple wood was found to average on 10 grms. by the Kjeldahl method 10.72 mgrms., and on 1 grm. by the micro method 1.065 mgrm.; and in apple wood extract 7.83 and 0.795 mgrm. respectively.

D. G. H.

Determination of Hoof Meal. **W. F. Sterling.** (*J. Assoc. Off. Agric.*

Chem., 1929, 12, 129-132.)—The mixture of hoof and horn, dried and ground, is known as hoof meal, and the quantity of hoof meal present in a mixture may be determined by adding sufficient chloroform or carbon tetrachloride to 1 grm. of sample (ground to pass a 40-mesh sieve) to float the meaty portion. The sediment of bone is drawn off, and the portion that floats is poured on to a filter with the solvent used, washed and dried. To this is added 50 c.c. of a solution of 0.1 *N* hydrochloric acid containing 1 grm. of pepsin U.S.P., and the mixture kept at 37-40° C. for 48 hours, after which 5 c.c. of 1 *N* sodium hydroxide is added and left for 10 minutes, when the mixture is centrifuged. The clear liquid is poured off, the residue washed with warm water and again centrifuged, and the process repeated several times, the final washing being with alcohol. The residue is dried and weighed and the weight multiplied by 1.54 gives the hoof meal. A microscopic examination of the residue should be made, and if vegetable tissue is present a correction is applied, if possible.

D. G. H.

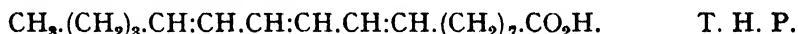
Organic Analysis.

Analysis by Means of the Thiocyanogen Value of Fats containing Linolenic Acid. Analysis of Linseed Oil. H. P. Kaufmann and M. Keller. (*Z. angew. Chem.*, 1929, 42, 20-23; 73-76.)—Comparisons of the iodine and thiocyanogen values of linseed oils after various periods and in the presence of various amounts of reagent have enabled the authors to formulate equations connecting the percentage contents of oleic (*O*), linolic (*L*) and linolenic (*Le*) acids with the total saturated fatty acids (*G*), and the iodine (*I*) and thiocyanogen (*T*) values. Elimination of impossible equations led to the conclusion that two out of the three double linkages of the linolenic acid, corresponding with $T=182.46$, are satisfied during the determination of the thiocyanogen value (ANALYST, 1928, 53, 613). The linseed oil to be analysed is saponified in the absence of oxygen, the unsaponifiable matter removed, and the fatty acids liberated, removed in pentane and well dried over freshly ignited sodium sulphate. The iodine value is then determined by the bromine method (*cf.* following abstract) with an excess of bromine solution (100 to 200 per cent.) for periods of 2 and 24 hours. The thiocyanogen value (*loc. cit.*) is determined on about 0.1 gm. of the acids, and in the presence of linolenic acid it is preferable to use a large excess (200 per cent.) of a 0.13 *N* solution of reagent and to titrate after 24 hours. The composition of the fatty acids is best obtained by Bertram's method (*loc. cit.* and *Z. Unters. Lebensm.*, 1928, 55, 179), which gives higher results than Twitchell's method. The following equations may then be solved:—(1) $G+O+L+Le=100$; (2) $89.93O+181.14L+273.70Le=100I$; (3) $89.93O+90.57L+182.46Le=100T$. The saturated portion of a mixture of the above acids is determined by the relation $G=100-1.100T$, but oleic acid may be replaced by other simple unsaturated acids (*e.g.* elaidic, erucic, petroselinic acids, etc.). A Calcutta linseed oil was found to have the following composition:—Saturated acids and unsaponifiable matter, 10.8; *O*, 11.9; *L*, 32.6; *Le*, 40.2; and glycerol residue 4.5 per cent. The literature of the subject is discussed critically, and the uses and advantages of the thiocyanogen value indicated. J. G.

Partial Halogen Addition to Unsaturated Fatty Acids. β -Elaeostearic Acid Glyceride and Wood Oil. H. P. Kaufmann and C. Lutenberg. (*Ber.*, 1929, 62, 392-401.)— β -Elaeostearic acid glyceride (m.pt. 60 to 61° C.) was prepared by exposure to light from the sun or quartz lamp of a solution of Hankow wood oil in pentane in the presence of solid iodine, and recrystallised from acetone. The addition of bromine to two double bonds of the glyceride and of natural wood oil was determined at 18° C. in the absence of light by titration, after various periods of time of a mixture of 30 c.c. of a 0.1 *N* solution of bromine and 10 c.c. of a solution of sample (about 0.12 gm.), both in pure carbon tetrachloride, with 0.1 *N* sodium thiosulphate solution. The iodine values, also, were determined by titration of the same mixtures in the presence of 25 c.c. of a 5 per cent. aqueous solution of potassium iodide, and it was shown that normally after 3 to 6 hours a

theoretical value was obtained in each case corresponding with the absorption of 2 mols. of bromine. For a normal oil variations in the amount of the excess of bromine has no influence. The "partial iodine value" was determined by the addition to about 0.1 grm. of sample in 15 c.c. of a mixture of equal volumes of chloroform and carbon tetrachloride of 20 c.c. of a 0.1 *N* solution of iodine in a 0.1 *N* solution of bromine in methyl alcohol saturated with sodium bromide. After 4 hours in the dark the mixture was titrated in the presence of potassium iodide. Comparative tests with the thiocyanogen value (*ANALYST*, 1928, 53, 613) showed that both for wood oil and for the glyceride the absorption corresponded with the saturation of one double bond, though the thiocyanogen value was usually 1 to 2 units higher than the partial iodine value for the same sample. (*Cf.* Toms, *ANALYST*, 1928, 53, 69.) J. G.

Constitution of α -Elaeostearic Acid, the most important Component of Chinese Wood Oil (Tung Oil). J. Böeseken. (*J. Soc. Chem. Ind.*, 1929, 48, 71-72T.)—Objection is raised to Steger and van Loon's statement that uncertainty exists in our knowledge of α -elaeostearic acid (*J. Soc. Chem. Ind.*, 1928, 47, 362T), the constitution of which has been proved, mainly by the investigations of the author and his collaborators, to be



Determination of the Iodine Value. II. Action of Iodine Chloride Solutions on Fatty Acids with Conjugated Double Linkings. E. T. Gelber and J. Böeseken. (*Rec. Trav. Chim. Pays-Bas*, 1929, 48, 377-385.)—For linolic acid, iodine values obtained after 2 hours' absorption correspond with only one double linking, and even when the action of Wijs's solution is continued for 18 hours, the value for two double linkings is not quite reached. Investigation shows that the reaction takes place in two stages; in the first, which is comparatively rapid, chlorine only is added at one of the double linkings, free iodine being separated, whereas saturation of the second double linking occurs only slowly. This behaviour is not peculiar to linolic acid and its esters, but is typical for higher fatty acids with conjugated double linkings. Similarly, with elaeostearic acid, two of the three double linkings are saturated quickly, whilst saturation of the third, even when a seven-fold excess of reagent is used, occupies some days. These results indicate that elaeostearic acid is a linolenic acid with conjugated double linkings. The above conclusions hold only for iodine chloride solutions, iodine bromide solutions reacting in a fundamentally different manner. T. H. P.

Insect Oils. M. Tsujimoto. (*J. Soc. Chem. Ind. Japan*, 1929, 32, 49B-54B.)—*Firefly Oil*.—The insects used were "Genji-hotaru" (*Luciola vitticollis Kiesenwetter*), and "Heike-hotaru" (*Luciola parva Kiesenwetter*), and after removal of the wings they yielded 4.8 per cent. of an orange-yellow viscous fat of iodine value 116. Of this, the fatty acids and unsaponifiable matter amounted to 85 per cent., consisting of 87 per cent. of fatty acids and 13 per cent. of unsaponifiable matter. The fatty acids had: M.pt., 36° C.; neutralisation value, 179.2; iodine value

(Wijs), 110.7; and ether-insoluble bromides, 17.9 per cent. The oil contained highly unsaturated acids. The unsaponifiable matter was a pale yellow soft crystalline mass, partly insoluble in petroleum spirit, the insoluble portion appearing to consist of an unknown higher alcohol. It was found that the head and thorax contained 1.5, and the abdomen 3.8 per cent. of oil (calculated on the whole insect), with iodine values 115 and 105, and n_D 1.4770 at 28.5° C. and 1.4732 at 29.5° C., respectively. The abdominal oil contained 18.65 per cent. of unsaponifiable matter.

Locust Oil.—On extraction with ether dried locusts (*Oxya japonica Willemse*) yielded 3 per cent. of dark greenish-yellow viscous oil having: Sp. gr. 18° C., 0.9688; acid value, 44.3; iodine value (Wijs), 122.6; saponif. value, 171.5; unsaponifiable matter, 15.75 per cent., of iodine value 91.8. The fatty acids (67.25 per cent.) showed: Neutralisation value, 196.0; iodine value, 150.8; ether-insoluble bromides, 37.4 per cent. (m.pt. 178° C. and containing 62.42 per cent. of bromine and therefore a hexabromostearic acid). The iodine value of the liquid acids (75 per cent.) was 187.7, and neutralisation value 189.2. The chief constituents of the fatty acids are C_{18} acids. By the digitonin method 44.1 per cent. of sterol was obtained from the unsaponifiable matter.

Cricket Oil.—The dried crickets (*Acheta mitrata*, *Burmeister*.) gave 2.4 per cent. of a dark brownish viscous oil showing: Sp. gr. at 19.5° C., 0.9312; acid value, 58.7; iodine value (Wijs), 116.0; sap. value, 181.5; unsaponifiable matter, 11.32 per cent. with iodine value 119.2. The fatty acids (78.73 per cent.) had iodine value, 124.3; neutralisation value, 202.4; ether-insoluble bromides, 6.9 per cent. (m.pt. 177–178° C. containing 62.13 per cent. bromine). By the digitonin method 45.45 per cent. of sterol (cholesterol) was obtained. D. G. H.

Determination of Neutral Fat in Sulphonated Oils. R. Hart. (*J. Amer. Leather Chem. Assoc.*, 1929, 24, 120).—The proportion of neutral fat is at present usually determined gravimetrically, but the author suggests that it is much more convenient and accurate to determine, in the usual manner, the saponification value corresponding to the glyceride, provided that the alcoholic solution is neutral to phenolphthalein, and that allowance is made for the fact that ammonia soaps in solutions of alcoholic potash behave like free fatty acids. The saponification value of the glycerides may be expressed as mgrms. of KOH per grm. or as percentage of free fatty acid. The saponification value of the original oil before sulphonation must have been determined previously. Possible error due to splitting off of organically combined sulphur trioxide during saponification is considered negligible. R. F. I.

Inorganic Analysis.

Absorption of Oxygen by Alkaline Pyrogallol. T. J. Drakeley and H. Nicol. (*J. Soc. Chem. Ind.*, 1929, 48, 62T).—The effect on the evolution of carbon monoxide of varying the concentration of potassium hydroxide from

0.05 *N* to 4 *N*, and the pyrogallol from 0.5 to 10 grms. per 100 c.c., is shown in this table :

Carbon monoxide evolved on oxygen absorbed (without agitation).

Normality of potassium hydroxide.	Concentration of pyrogallol per 100 c.c.					
	0.5 gm. Per Cent.	1.0 gm. Per Cent.	2.5 grms. Per Cent.	3.5 grms. Per Cent.	5.0 grms. Per. Cent.	10.0 grms. Per Cent.
0.05	—	0.1	0.7	—	0.4	—
0.10	—	0.6	0.4	—	—	—
0.20	3.1	—	0.55	0.4	0.4	—
0.25	—	—	0.65	—	—	—
0.40	3.5	3.3	0.95	0.75	0.5	—
0.67	—	—	3.2	2.65	—	—
0.80	3.75	3.65	3.4	3.2	0.9	0.55
1.2	—	—	4.6	3.8	—	—
1.5	6.5	6.0	5.2	—	3.2	0.85
2.2	—	8.5	7.1	—	—	—
2.5	—	—	—	7.0	—	—
3.0	—	9.9	7.9	7.3	6.7	—
4.0	—	8.5	7.5	—	5.9	—

It is seen that the carbon monoxide evolved increases with the concentration of the alkali, but decreases with the concentration of the pyrogallol. If curves are plotted of percentage carbon monoxide evolved against normality of alkali, peculiar shapes of curve are obtained, which show no stoichiometrical relationship between the two functions. Agitation during oxygen absorption decreases the evolution of carbon monoxide in solutions of higher concentration, but not in concentrations below 0.6 *N* alkali and 2.5 grms. of pyrogallol per 100 c.c. An absorption made with agitation in a very old solution was always found to give a lower percentage of carbon monoxide than an absorption made without agitation in a fresh solution of the same composition.

R. F. I.

Iodimetric Determination of Chromium (Chromic Oxide) in Chrome Alum. J. E. S. Han. (*J. Amer. Leather Chem. Assoc.*, 1929, 24, 124.)—In the ordinary determination of chromium by oxidising the potash chrome alum solution with sodium peroxide, followed by the decomposition of excess and treatment with acid and potassium iodide, two sources of error are possible. One is the presence of iron in the chrome alum which will give results too high by liberating iodine, and the other is insoluble matter in the peroxide, which, on treatment with acid, will produce hydrogen peroxide, decomposing its equivalent of chromic acid, thus giving results too low. Both errors may be overcome by filtering the oxidised, well-boiled alkaline solution before acidification. With chrome alums containing as much as 0.5 per cent. of ferric oxide one filtration is found to be enough, the amount of chromium co-precipitated with the iron being negligible. The amount of iron in the precipitate may, if required, be readily determined after washing it free from sodium chromate.

R. F. I.

Determination of Bismuth. G. J. Hough. (*Chemist Analyst*, 1929, 18, 3-4.)—A solution in *aqua regia* of 0.5 gm. of the sample is neutralised with ammonia, an excess of ammonium sulphide added, and the precipitate filtered after 5 minutes on the water bath. It is then washed, dissolved in 10 c.c. of nitric acid and 50 c.c. of hot water, and the bismuth reprecipitated from the filtered solution by ammonia, filtered, redissolved in dilute sulphuric acid, and boiled for about 30 minutes with a small square of aluminium foil. When reduction is complete the aluminium is removed, the metallic bismuth dissolved in 10 to 15 c.c. of warm, saturated ferric chloride solution, and titrated in the presence of 200 c.c. of cold water and 5 c.c. of syrupy phosphoric acid (sp. gr. 1.7) with 0.1 *N* potassium permanganate solution standardised under similar conditions. Lead in small quantities may be removed as sulphate. Satisfactory agreement with the gravimetric and molybdate methods was obtained with ores containing antimony, arsenic, copper, and silver. J. G.

Action between Copper Salts and Glycerol. B. K. Vaidya. (*Nature*, 1929, 123, 414.)—Vigorous action occurs when glycerol solutions of copper salts are heated to 150–200° C., the salts (except cupric chloride) being decomposed into fine metallic copper of over 99 per cent. purity and free acid, which may decompose further. In the case of cupric chloride, crystalline cuprous chloride is quantitatively formed, probably as the result of a secondary reaction. Almost the same result is obtained with other polyhydric alcohols, such as glycol, erythritol, and mannitol. It appears likely that a copper compound of the type $C_6H_{10}O_6Cu_3$ is first formed and later undergoes decomposition into copper, carbon dioxide, methane, and, possibly, ethane. The reaction serves for the preparation of copper highly suitable for catalytic purposes, even crude copper sulphate giving a good product. T. H. P.

Sodium Alizarinsulphonate as a Reagent. F. G. Germuth and C. Mitchell. (*Amer. J. Pharm.*, 1929, 101, 46–52.)—The reagent (0.3 c.c. of 0.5 per cent. solution) was added to 5 c.c.-portions of one per cent. solutions of metallic chlorides or nitrates. Precipitates of some shade of red were obtained in the case of lead, mercury⁺, bismuth, copper, antimony^v, tin⁺, iron⁺, cobalt, magnesium, aluminium, and platinum⁺. The precipitates with cadmium and tin^{iv} were orange; chromium, yellow; iron⁺⁺⁺, smoky black; uranium, deep violet; thallium, dark blue; and titanium⁺⁺⁺, black. Soluble compounds of a red shade were obtained with barium, strontium, calcium, zinc, nickel, and gold solutions. The same precipitates were obtained at a dilution of 0.01 per cent. of the reacting salts, by addition of 0.1 c.c. of reagent and one drop of 5 per cent. ammonia. Most of the metals still gave a precipitate at a concentration of one part of salt in 1,000,000 of water. W. R. S.

Detection of Vanadium. A. Fölsner. (*Chem. Zeit.*, 1929, 53, 250.)—The hydrogen peroxide test was found to be unreliable for minute quantities (*cf.* ANALYST, 1926, 595). The author gives preference to lead acetate as a reagent.

For the detection of vanadium in steel, the *aqua regia* solution is evaporated to dryness, the silica filtered off, and the iron precipitated with an excess of caustic soda. The alkaline filtrate is acidified with acetic acid, and a solution of lead acetate added; a faint but distinct turbidity was obtained at a concentration of 0.03 grm. V. per litre (but cf. Evans and Clarke, *ANALYST*, 1928, 53, 475).

W. R. S.

Physical Methods, Apparatus, etc.

Absorption Spectra and Fluorescence of Fats. H. P. Kaufmann. (*Chem. Umschau*, 1929, 36, 34–35.)—The recent advances in the subject are discussed with special reference to a paper by Sproesser (*id.*, 1928, 35, 325) and to the author's step photometer (*Z. angew. Chem.*, 1928, 41, 1123), which is recommended for the quantitative measurement of luminescence. It is concluded that absorption spectra measurements are of little use for the identification of foreign substances in cacao butter, though they may prove of service with pure substances. For example, it was shown that the selective absorption of the elaeostearic acids was of a distinctly different type from that of linolic acid; therefore the former does not contain two unsaturated linkages (cf. Andant, *Compt. rend.*, 1927, 184, 1068; and Weiss, *ANALYST*, 1929, 178). J. G.

Fluorescence of Colouring Matters in Ultra-Violet Light. A. Seyewetz and J. Blanc. (*Comptes rend.*, 1929, 10, 714–715.)—Colours showing in aqueous or aqueous-alcoholic solutions a clear and characteristic fluorescence fall into the following classes: diphenyl methane derivatives; auramines and pyronines; triphenylmethane derivatives; phthaleins and some rosaniline derivatives; thio-benzenylic derivatives; primuline and thioflavines; quinoline and acridine derivatives; quinoline yellow and red, and acridine yellow and orange; fluorescent compounds resulting from diazotising and interacting of already fluorescent substances. Fluorescence of halogen derivatives of fluorescein diminishes from chloride to iodide, and with the number of substituted halogen groups. For a given colour fluorescence varies according to the solvent. The fluorescence of dyed fibres diminishes rapidly with increase of colour fixed, and varies in colour with the nature of the fibre. D. G. H.

New Melting-point Apparatus. F. Kerchow. (*Chem. Zeit.*, 1929, 53, 219.)—This is a modification of Hosking and Short's apparatus (*ANALYST*, 1926, 51, 270). The bulb of the thermometer, with the capillary-tube containing the substance, dips into a small paraffin-oil bath, as only in this way can identity of temperature between substance and thermometer be ensured. The vertical tube in which the thermometer is suspended is surrounded by an air-jacket open at the bottom, and the steady air-current is heated by a coil of resistance wire, having a resistance of about 7 ohms, inserted in the horizontal portion of the tube. The heating current is controlled with the help of an ammeter and an external resistance,

so that, when the melting-point is approached, the rate of temperature-rise may be adjusted to 1° in one or two minutes. With an air-current of 950 litres per hour and a heating current of 6 amperes, 100° C. is reached after 4 minutes and 200° C. after 10 minutes; with 7 amperes, 300° C. is reached in 16 minutes. After shutting off the heating current, the temperature rises a further 30° from 100° , 11° from 200° , or 5° from 300° C. The current necessary to cause a rise in temperature of 1° in 1-2 minutes is 1.5 amperes at 50° , 2.8 at 100° , 4 at 200° , or 6 at 300° C. These data should be determined for the particular apparatus used, so that the initial current of 6 or 7 amperes may be shut off at the right time and the proper current to give the slow temperature-rise started when the after-heating has nearly ceased.

T. H. P.

Reviews.

DIE CHEMISCHE ANALYSE. Edited by Dr. B. M. MARGOSCHES. Vol. XXVI. DIE VISUELLE LEITFÄHIGKEITSTITRATION UND IHRE PRAKTISCHEN ANWENDUNGEN. Prof. Dr. G. JANDER and Dr. O. PFUNDT. Pp. 64+viii. Stuttgart: Ferdinand Enke. 1929. Price 9s.

There are two classes of electrometric titration, the potentiometric method and the conductometric method. In the former the change in potential of a suitable electrode immersed in a solution containing its ions is determined after the addition of various amounts of reagent, whilst in the latter it is the change in resistance or conductivity of the solution that is measured. Potentiometric titration is of course widely used, but its limitations and pitfalls are only too familiar to those who use it, and it is surprising that conductometric measurements are not more extensively adopted as supplementary methods, or, in certain cases, even as alternatives. This apparent neglect is probably due to the fact that since, in order to avoid electrode polarisation, alternating currents must be used for conductivity measurements by the Wheatstone bridge method, an A.C. instrument is required to indicate the point of zero current. A.C. indicating instruments are usually less sensitive than the D.C. type, and though the ordinary telephone may give quite accurate results it has certain obvious disadvantages, particularly when rapidity is required. The popularisation of wireless, however, has recently led to the production of crystals and rectifying valves as commercial articles, and by rectification of the current by these or similar means the ordinary sensitive D.C. indicating instruments may be used. Hence the so-called "visual method."

This small volume, which is the twenty-sixth of the series on Chemical Analysis edited by Dr. B. M. Margosches, deals with this important method in a clear and concise manner. The advantages of conductometric over potentiometric titration in certain cases and the limitations of the telephone method are

indicated, and useful hints are provided for the construction of an apparatus with the maximum sensitiveness. The author favours the iron-constantan thermocouple by means of which the heating effect of an A.C. current is translated into millivolts. Nevertheless, more space might well have been devoted to the valve rectifier, as this is widely used. The crystal detector, also, in spite of its instability, provides a cheap and efficient method for rectification, and some recommendation as to the best type for the purpose would have been welcome. Carborundum is preferred by many workers. An induction coil is, of course, the obvious means of providing A.C. current, but where a steady supply is required an oscillator is very suitable, and a description of one of these instruments would also have been very useful.

After a short chapter on the choice of reagents and the influence of impurities, a number of typical titrations are described. These include acidimetry, alkalimetry, the determination of iron, and of chlorides and sulphates (*e.g.* in drinking water). Ammonium salts (*e.g.* in fertilisers) may be titrated with a strong base by this method, and conversely, salts of weak acids may be displaced by strong acids. The determination of potassium is dealt with at length, and the method appears rapid and sensitive, and may be used in the presence of sodium. An attempt is also made to apply the method to the routine testing of milk, though the more familiar determination of the ash content of sugar solutions is not mentioned.

On the whole, it seems that, from an analytical point of view, great possibilities exist for applications of conductometric titration. At present, however, apart from straightforward determinations of single substances, the analyst will usually have to work out the procedure or standardise the apparatus for a particular case. The volume will perform a service in bringing before the analyst a somewhat neglected aspect of electrometric titration.

The book is rather expensive for its size, though the high standard of production of the other volumes of the series is maintained. A misprint occurs on p. 43, where the ferric ion is represented as $\text{Fe}^{..}$.

JULIUS GRANT.

APPLIED CHEMISTRY. By C. K. TINKLER and H. MASTERS. Volume I. WATER, DETERGENTS, TEXTILES, FUELS, ETC. Second edition, revised. xi+296. With 34 illustrations and 2 plates. London: Crosby, Lockwood & Son. 1929. Price 15s. net.

This volume, the previous edition of which was reviewed in this Journal (1920, 45, 346), is intended as a textbook principally for the use of third-year students of chemistry who propose taking a degree in public health or household and social science. The principal title is perhaps somewhat misleading, since it is suggestive of an enormously greater field than that covered by the text.

The subject-matter comprises an admirable selection of methods for sampling, and for the chemical and physical analysis of a variety of materials from a hygienic

and economical standpoint, together with concise theoretical explanations where necessary. That the authors possess a wide knowledge of the students' requirements is evident from their judicious experimental instructions, which are so complete that but little assistance from the demonstrator should be necessary, even in such a determination as the calorific value of coal.

Among other notable features of the volume are the numerous references to other pages and to various textbooks and reports in which fuller information may be found.

Much care has been expended on the elimination of errors both from the text and the index, with the result that very few adverse criticisms are called for, but in practice little difference in the result is obtained whether the temporary hardness of a water is determined by soap solution or by titration with standard acid, although a sentence on p. 25 tends to contradict this. The estimation on p. 40 is liable to yield low results owing to partial solution of the silica on addition of water after evaporation to dryness. Heating of the residue to 250° C. is essential if this is to be avoided. In Fig. 3 the small tube C would hardly contain sufficient dilute acid to decompose the 1 gm. of solid used for the estimation, unless the remainder of the apparatus was inconveniently bulky. Apart from a very few insignificant typographic errors, the remainder of the volume is free from fault, although some readers may take exception to the term "microphotographs" being used for the very excellent series of photomicrographs depicting textile fibres on the two plates. The former expression is generally applied to minute photographs of large objects. The volume is altogether an extremely useful and valuable production, the typescript, illustrations, and index being complete and reliable, whilst the general style throughout is a testimony to the care expended upon it by both the authors and publishers. To the reviewer the only undesirable and practically useless feature present is the 16 pages of advertising matter inserted at the end of the volume where the index should be placed.

T. J. WARD.

CHEMISTRY IN MEDICINE. Pp. xxii+757. 8vo. New York: The Chemical Foundation, Inc. 1928. Price \$2.

This book is the result of a co-operative effort among nearly 50 biologists, chemists and medical men, to present to the American public "the great possibilities for advance in medical science through further intensive co-operation between chemistry and medicine." It is hoped by this means to produce chemical uplift in the non-Elect and that the uplifted will duly see to it that still more dollars are devoted to this kind of research. It may seem odd to men of science in poverty-stricken Europe, who read so frequently of what seem to them magnificent donations to universities and similar bodies in the United States, that these institutions should need more money, but Dr. J. Stieglitz, the editor of this volume, and his five associate editors, assure the reader that this is the case.

This is by far the best of a number of books written in recent years to explain to the ordinary man what science, and especially chemistry, has done for him. In the reviewer's experience the ordinary man remains blissfully ignorant of the existence of such literature, even when he is "high-brow" enough to read and appreciate H. G. Wells, de Kruif, Sinclair Lewis, Pierre Hamp, or Aldous Huxley, whose works sometimes carry a scientific atmosphere, and even upon occasion bristle with scientific terms.

One can imagine those figments of Mr. Sinclair Lewis's imagination, "Mr. Babbitt" and "The Man who knew Coolidge," struck by the caption "Heredity and Development" in this volume, starting to read Prof. Alexander Weinstein's interesting, but rather technical article, on this subject. In the fifteenth line they meet the word "cytoplasm," and in the 17th the term "chromosomes." Will they consult the glossary, which the editors have thoughtfully provided, and carry on, or will they give up in despair? This is not a criticism of Dr. Weinstein's article; it is a mere statement of the difficulty he and his colleagues have made a gallant effort to overcome. This effort may fail in its immediate objective of reaching the general public, but it may still produce great effects indirectly, for the book can hardly fail to interest chemists, biologists and medical men in the necessity of somehow or other finding means of awakening public concern in these matters.

The book is no mere recital of the successes achieved by chemists in the production of synthetic drugs, though these receive due attention, but covers such fundamental matters as the work of the physiologist and the biochemist on heredity and development, metabolism of the body, problems of nutrition, dietary diseases, and hormones; and the work of the chemist in safeguarding water and food supplies, devising means for the disposal of sewage and providing protection against industrial disease. In a series of fascinating articles constituting the last two sections of the book, the present position of work on the great parasitic diseases, malaria, amoebic dysentery, leprosy, hookworm, syphilis and tuberculosis is outlined, and Dr. Voegtlin explains why chemotherapy is a hope of mankind.

The articles are not all of equal merit; they overlap here and there, and some of their authors are unduly impressed with American achievements which do not look quite so important on this side of the Atlantic, but taken altogether, the editors and contributors have done their work admirably, and if they fail to reach and interest the general public it is not for want of earnest endeavour on their part.

British readers will note with pleasure the tributes paid to the work of many of their countrymen throughout the book, and when Dr. Voegtlin points out that chemistry is called upon to save Africa they will no doubt remember that a good slice of Africa is included in the British Empire, and that it is their job to supply the chemistry.

T. A. HENRY.

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- A TEXTBOOK OF BIOCHEMISTRY. By A. T. CAMERON. London: J. & A. Churchill. Price 15s.
- INORGANIC QUANTITATIVE ANALYSES. By H. A. FALES. London: G. Bell & Sons. Price 12s. 6d. net.
- THE ABC OF VITAMINS. By J. PRYDE. London: John Hamilton, Ltd. Price 2s. 6d. net.

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, May 1st, the President, Mr. Edward Hinks, being in the chair.

Certificates were read for the first time in favour of:—John William Haigh Johnson, M.Sc., F.I.C., Mamie Olliver, B.Sc., A.I.C., and George Edward Shaw, B.Sc.

Certificates were read for the second time in favour of:—Alfred Norman Leather, B.Sc., F.I.C., Richard Harold Morgan, B.Sc., A.I.C., and William George Painton, B.Sc., A.I.C.

The following were elected Members of the Society:—Peter Trevisa Clarke, B.A., Alfred Clive James, B.Sc., A.I.C., Herman Lee, B.Sc., A.I.C., James Frederick Morse, Lawrence John Odling, Willie Horner Wilkinson.

The following papers were read and discussed:—"The Determination of Organic Peroxides," by R. S. Morrell, M.A., Ph.D., F.I.C., and S. Marks, M.Sc., A.I.C.; "Differential Halogen Absorption of Oils and Fats," by J. W. Croxford (Work done under the Analytical Investigation Scheme); "A New Method for the Separation of Small Quantities of Tantalum and Niobium from Titanium," by W. R. Schoeller, Ph.D., and C. Jahn (Work done under the Analytical Investigation Scheme); and "The Analysis of Small Samples of Gas," by H. R. Ambler, B.Sc., A.I.C.

The Alkaloid Test for Tannins.

BY CHRISTINA MARY FEAR, B.Sc.

(*Work done under the Analytical Investigation Scheme.*)

(*Read at the Meeting, March 6, 1929.*)

F. A. A. MEYER (*Crell's Ann. Chem.*, 1791, Part I, 43) seems to have been the first to have recorded the observation that an infusion of cinchona bark is precipitated by an infusion of gall nuts. This was confirmed by Duncan (*Nicholson's J.*, 1803, 6, 225), Fourcroy and Vauquelin (*Bull. Pharm.*, 1810, 2, 241), Pelletier and Caventou (*Ann. Chim. Phys.*, 1820, 15, 2891), and Henry and Plisson (*J. Phar.* 1827, 13, 268). Later, the use of quinine as a reagent for the detection of tannins was suggested by Pelouze (*Ann. Chim. Phys.*, 1834, 57, 423), and this base was subsequently referred to as Pelouze's reagent by Henry (*J. Pharm.*, 1835, 21, 213), who made the sweeping statement that all alkaloids are precipitated by tannins, a view now widely accepted by workers on tannin chemistry. In the course of some work carried out by Mr. A. E. Jones in this laboratory it was, however, noticed that pilocarpine was not precipitated by gallotannin, and at the suggestion of Dr. Nierenstein an investigation was undertaken to see how far the generally accepted view is correct.

The following table gives the results obtained by using a 1 per cent. gallotannin solution, made up as follows:—The weighed gallotannin was washed into a graduated flask with hot distilled water until all had dissolved, the solution was cooled, and made up with cold water. All alkaloids investigated were obtained from the British Drug Houses in the form of their hydrochlorides; experiments were carried out at room temperature.

The following results were obtained on adding 2 c.c. of 1 per cent. gallotannin solution to the different alkaloids:—(*See table on next page.*)

This tannin was a commercial specimen of Schuchardt's gallotannin from Chinese galls. As a check, further experiments were made with pilocarpine and papaverine hydrochlorides, the following gallotannins being used:

- (1) Schuchardt's gallotannin, purified according to Emil Fischer's method.
- (2) Mitchell's gallotannin (*i.e.* gallotannin practically free from glucose).
- (3) A specimen of gallotannin prepared from Basra galls (Aleppo gallotannin) in this laboratory (*i.e.* gallotannin which contains ellagic acid in addition to gallic acid in its molecule).

The results were identical in all cases.

CONCENTRATION OF ALKALOID SOLUTION.

Alkaloid.	CONCENTRATION OF ALKALOID SOLUTION.					
	10 per cent.	Saturated below 10 per cent.	1 per cent.	Saturated below 1 per cent.	0.1 per cent.	0.01 per cent.
Aconitine.	No ppt.		No ppt.		No ppt.	No ppt.
Apomorphine.	"		"		"	"
Atropine.	Very slight opalescence.		Very slight opalescence.		"	"
Berberine.				No ppt.		
Betaine.	No ppt.		No ppt.		No ppt.	No ppt.
Brucine.	Heavy white curdy ppt.		Heavy white curdy ppt.		Heavy white curdy ppt.	Heavy white curdy ppt.
Caffeine.	Heavy white curdy ppt.		Heavy white curdy ppt.		Heavy white curdy ppt.	No ppt.
Cinchonidine.		Heavy yellowish white colloidal ppt.	White colloidal ppt.		White colloidal ppt.	Very slight opalescence.
Cinchonine.		Heavy yellowish white colloidal ppt.	Heavy yellowish white colloidal ppt.		Yellowish white colloidal ppt.	No ppt.
Cotarnine.	Very slight opalescence.		Very slight opalescence.		No ppt.	No ppt.
Emetine.	Slight opalescence.		Slight opalescence.		Slight opalescence.	Slight opalescence.
Ephedrine.	Very slight opalescence.		Very slight opalescence.		No ppt.	No ppt.
Homatropine.	No ppt.		No ppt.		No ppt.	No ppt.
Hydrastine.	Slight opalescence.		Slight opalescence.		Very slight opalescence.	Very slight opalescence.
Hydrastinine.	No ppt.		No ppt.		No ppt.	No ppt.
Narceine.				Slight opalescence.		
Narcotine.	No ppt.		No ppt.		No ppt.	No ppt.
Papaverine.	"		"		"	"
Pilocarpine.	"		"		"	"
Quinine.	Heavy yellowish white flocculent ppt.		White colloidal ppt.		White colloidal ppt.	Slight opalescence.
Strychnine.	Heavy white curdy ppt.		Heavy white curdy ppt.		Heavy white curdy ppt.	Heavy white curdy ppt.
Tropacocaine.	No ppt.		No ppt.		No ppt.	No ppt.
Yohimbine.	"		"		"	"
Cocaine.	Very slight opalescence.		Very slight opalescence.		"	"
Dimorphine.			Sat. at 1 per cent.			
Morphine.			No ppt.		"	"

From these experiments it is evident that the only alkaloids giving appreciable precipitates with tannin solutions are brucine, caffeine, cinchonine and cinchonidine, quinine and strychnine. The possible relationship between the structure of alkaloids and their precipitation by tannins opens up an interesting field of speculation. Moreover, it seems probable that the phenomenon described as precipitation is one of interaction (either physical or chemical) of alkaloid and tannin; and is not due to precipitation of unchanged alkaloid hydrochlorides

through supersaturation. This is supported by the fact that intensity of precipitation does not vary from 1 per cent. to 10 per cent. solutions. If the reaction were merely one of supersaturation, those alkaloids showing opalescence in 1 per cent. solution might be expected to give a definite precipitate, or, at least, a decided increase in opalescence in 10 per cent. solution.

The assumption that the alkaloids are general reagents for the tannins has evidently to be modified.

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DISCUSSION.

The PRESIDENT said that this was an interesting piece of work done under the Analytical Investigation Scheme. It was a valuable contribution because it systematically examined and, to a certain extent, refuted a statement which was largely and generally accepted about the precipitation of all alkaloids. The only thing which struck him was that all the precipitations were made in neutral solutions, and there were some alkaloids, he thought, which were not precipitated in neutral solution, but were in acid solution; he suggested that the work might possibly be extended to determine the precipitability in various acid solutions.

The Refraction of Milks Low in Solids-not-fat.

BY G. D. ELSDON, B.Sc., F.I.C., AND J. R. STUBBS, M.Sc., F.I.C.

(Read at the Meeting of the Northern Section, March 1, 1929.)

ABOUT two years ago (ANALYST, 1927, 52, 193) we gave an account of our experience with the refractometer as a weapon for the detection of added water in milk, and later (*id.*, 1928, 53, 150) gave some supplementary results supporting the conclusions at which we had arrived as the result of our previous work.

It has been stated that the method is very useful and reliable in cases of the type:—Fat, 3·2; solids-not-fat, 8·2; ash, 0·7 per cent.; refraction of copper serum, 38·5 at 20° C.

We have already dealt with one aspect of this claim in a recent paper (*Chem. and Ind.*, 1928, 47, 1145), and we now offer the result of a further year's observations in continuation of our work on this subject.

During the year 1928 we have examined some 2850 samples of milk, and have observed the refraction of a considerable number of these. This number has included all those in which the solids-not-fat were less than 8·5 per cent.

It is interesting to examine the figures we have obtained on the analysis of the whole of the milks received during the year having less than 8·5 per cent. of solids-not-fat. A few milks with solids-not-fat of 8·5 per cent. have been included, and in every case where a corresponding "appeal-to-cow" sample has

been obtained the figures for this are given for comparison. The "acidity" is the number of c.c. of 0.1 N sodium hydroxide solution per 10 c.c. of milk.

ORIGINAL SAMPLE.					"APPEAL-TO-COW" SAMPLE.			
Date.	Fat.	Acidity.	Solids-not-fat.	η	η	Solids-not-fat.	Acidity.	Fat.
Jan. 10	3.3	2.2	8.0	36.6	37.7	8.6	2.6	3.7
" 27	2.4	1.6	7.0	33.8	37.2	8.4	2.0	3.2
Feb. 7	3.6	2.0	8.2	36.9	—	—	—	—
"	3.8	1.9	8.0	36.5	37.7	8.7	2.2	3.5
"	2.3	2.0	7.9	35.7	38.2	8.6	2.2	3.7
" 17	3.1	2.1	8.0	36.3	38.4	8.9	2.6	3.2
" 23	3.3	1.9	8.1	36.3	38.2	9.1	2.1	3.3
" 29	2.4	1.7	7.8	35.6	37.4	8.4	2.0	2.1*
Mar. 6	2.8	1.7	8.1	36.7	37.4	8.6	2.1	2.8
" 15	3.0	1.7	7.4	35.0	37.8	8.5	2.4	3.3
" 21	2.6	2.8	7.5	35.5	37.4	8.4	2.3	3.1
"	3.6	2.5	7.8	36.5	37.6	8.4	2.9	4.0
April 11	3.2	1.9	8.3	37.5	—	—	—	—
"	3.3	2.0	8.2	37.4	—	—	—	—
" 12	3.4	2.2	8.1	35.7	38.8	9.0	2.9	4.0
" 23	2.4	1.6	7.5	34.4	37.9	8.8	2.1	3.7
" 24	3.7	2.2	8.3	36.8	37.7	8.5	2.5	2.6
"	2.6	2.2	8.5	36.6	37.5	8.6	2.2	2.5
"	4.0	2.1	7.9	36.1	38.0	8.6	6.0	3.2
May 7	3.4	—	8.2	36.5	—	—	—	—
June 21	2.9	2.1	8.3	36.4	—	—	—	—
July 18	3.0	2.1	8.3	36.6	37.6	8.7	2.1	3.0
" 23	3.2	1.8	8.0	36.5	37.9	8.5	1.8	3.7
" 24	3.1	1.6	8.0	36.3	38.8	8.7	5.8	3.3
"	2.8	1.6	8.4	36.8	—	8.4	—	2.7
" 26	2.8	1.6	7.6	35.0	38.7	9.0	2.0	4.1
" 27	3.5	1.8	8.3	37.0	—	—	—	—
"	4.0	1.7	8.1	36.9	—	—	—	—
Aug. 16	3.4	1.7	8.2	36.9	—	—	—	—
"	3.0	1.8	8.3	37.1	—	—	—	—
" 28	3.2	1.9	8.1	36.8	37.6	8.7	2.2	3.3
Sept. 14	3.5	1.6	7.8	35.3	38.8	9.2	2.0	3.6
" 21	3.0	1.8	8.6	36.5	—	—	—	—
" 26	3.0	1.5	7.6	34.8	38.2	9.0	2.2	3.7
Oct. 5	3.5	1.8	8.1	35.8	—	—	—	—
"	4.0	1.7	8.5	37.0	—	—	—	—
" 8	3.2	2.0	7.1	34.3	37.0	8.3	2.2	3.8
" 9	3.6	2.0	7.8	36.3	36.0	7.8	1.6	3.6*
Nov. 14	4.0	1.7	8.3	36.7	—	—	—	—
" 15	3.2	1.9	6.4	32.5	37.8	8.7	2.0	4.5
"	3.0	2.8	6.8	33.4	37.8	8.9	2.3	3.6
"	3.4	2.0	8.2	36.3	—	—	—	—
"	3.2	2.0	8.4	37.0	—	—	—	—
" 23	3.9	6.2	8.2	38.3	—	—	—	—
"	3.2	4.5	7.8	36.6	39.0	8.5	5.5	4.9
"	3.3	3.8	8.1	37.4	39.0	9.1	3.0	3.9
"	2.8	4.1	8.2	37.9	39.0	9.0	2.8	3.5
Dec. 13	2.2	2.1	8.1	36.6	—	—	—	—
" 21	4.0	1.9	8.0	35.9	—	—	—	—
"	3.5	2.0	8.2	36.3	—	—	—	—
"	4.2	2.1	8.1	36.4	—	—	—	—

* One cow.

From an examination of this table it will be seen that in every case (except two, which are dealt with below) a low solids-not-fat corresponds with a low refraction. This means one of two things—or possibly a combination of both.

Either all the low solids-not-fat are due to watering or to the fact that milks naturally low in solids-not-fat do not give a normal refraction of 38 or more. It must be emphasised that our own results were obtained from 2850 samples of mixed milks, and that we have now examined in all well over 8000 samples with similar results.

The figures for the first and fourth samples received on November 23 agree very closely with those given in paragraph two above. Objection may, therefore, be taken that these samples do not conform to our contention that a milk having a low solids-not-fat will have a low refraction. Such a conclusion would, however, be quite unjustifiable, for these samples actually illustrate quite well the point we tried to establish in our paper in *Chem. and Ind. (loc. cit.)*. Both samples had become sour before examination, and the high refractions are to be attributed to this fact. No "appeal-to-cow" sample was taken in connection with the first sample, but, in the case of the fourth, watering was certainly proved by this means.

In those cases where "appeal-to-cow" samples were taken, the refraction of these was greater than that of the original sample in every case except one. This was found to be milk from an individual cow, and all the figures agreed well with those of the original sample, proving that no water had been added and that a milk naturally low in solids-not-fat may give a low refraction.

Investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates.

XIV. A New Method for the Separation of Small Quantities of Tantalum and Niobium from Titanium.

BY W. R. SCHOELLER, PH.D., AND C. JAHN.

(Work done under the Analytical Investigation Scheme.)

(Read at the Meeting, May 1, 1929.)

THIS Section marks a further advance in our quest for a reliable quantitative method for separating titanium from tantalum and niobium. In Section IX (ANALYST, 1927, 625), Schoeller and Deering have shown that, when a solution of the tartaric complexes of the metallic acids is boiled with a large excess of mineral acid, the earth acids are precipitated, whilst titanate salt remains in solution ("tartaric hydrolysis method"). The separation is approximate, because the earth acids are not quite quantitatively precipitated and the precipitate occludes titania. Now, whereas the titania content of the earth-acid precipitate can be

reduced to a very small figure by one or two repetitions of the procedure, the recovery of the small amount of earth acid that accompanies the titania into the filtrates is a much more arduous problem. The task we set ourselves was to discover a method capable of recovering a small amount of earth acid in presence of a relatively large quantity of titania; in other words, a supplementary procedure that would resolve into its constituents the titania fraction from the tartaric hydrolysis process.

What seemed the most promising point of attack was to utilise the ready formation of a soluble titanium complex of one of the aromatic hydroxy-compounds (*cf.* Hauser and Lewite, *Ber.*, 1912, **45**, 2481). Muller attempted a quantitative separation by means of salicylic acid, but his method, involving a number of re-treatments, was proved by Schoeller and Deering (*loc. cit.*) to result in loss of earth acid at each repetition of the procedure. After many fruitless attempts with a variety of reagents (see final paragraph) we eventually modified and greatly improved a method (the principle of which was evolved by one of us in 1923) hereafter designated as the "oxalate-salicylate method."

TARTARIC HYDROLYSIS METHOD FOR SMALL QUANTITIES OF EARTH ACIDS.—Before describing the oxalate-salicylate method we will give some necessary details of tartaric hydrolysis on a small scale, as this forms the final stage of our new process.

Procedure.—The oxides are fused with 0.25 grm. of potassium bisulphate in silica, and the product dissolved in a hot strong solution of 0.25 grm. of tartaric acid. The liquid is transferred to, or filtered into, a small beaker, and treated while boiling with 5 c.c. of strong nitric acid, the total bulk being 25 to 30 c.c. After 5 to 15 minutes' boiling, the beaker is allowed to stand a few hours, the precipitate mixed with a little filter pulp, collected, washed with dilute ammonium nitrate solution, ignited wet, and weighed as $(\text{Ta}, \text{Nb})_2\text{O}_5$. The results are given below (initial bulk, 30 c.c.):

Exp.	M_2O_5 taken. Grm.	TiO_2 added. Grm.	Precipitate formed:	M_2O_5 recovered. Grm.
1	0.0009	—	after 15 minutes' boiling	0.0003
2	0.0030	—	" 3-4 " "	0.0030
3	0.0060	—	" 2 " "	0.0060
4	0.0090	—	at once	0.0090
5	0.0010	0.0050	after 15 minutes' boiling	0.0004
6	0.0035	0.0054	" 4 " "	0.0030
7	0.0060	0.0055	" 2 " "	0.0059
8	0.0090	0.0057	at once	0.0091

As shown by these tests, the quantitative recovery of the earth acids is practicable, provided the dilution is not excessive: serious negative errors occurred only in Exps. 1 and 5, with an initial M_2O_5 concentration of 0.03 mgrm. per c.c. A minimum concentration of 0.1 mgrm. should be aimed at; on the other hand, the concentration should not be too high (*e.g.* above 1 mgrm. per c.c.), because

precipitation would be too sudden, the precipitate being more slimy than flocculent and occluding titania, if present (*v. infra*, Exp. 17). The recovered M_2O_3 must be fused with bisulphate, and the melt dissolved in a warmed mixture of hydrogen peroxide and sulphuric acid; any yellow tint is matched against that produced by a standard titanium solution, and the necessary correction made.

When carried out with the precautions here given, tartaric hydrolysis on a small scale is an eminently satisfactory precipitation reaction of the earth acids: a fraction of a mgrm. is readily recovered from a bulk of about 2 c.c. by boiling with 1 c.c. of nitric acid. At the same time, a good separation from titania is achieved.

THE OXALATE-SALICYLATE METHOD.—When a solution containing the oxalates of titanium and ammonium and a small quantity of oxalo-earth acids is treated with an excess of sodium salicylate, the characteristic orange colour of the salicylic titanium complex is produced. If now the oxalic ion is removed from the solution by addition of calcium chloride, the bulky oxalate precipitate carries down the earth acids whilst the titanium complex remains unaffected. The precipitation of the earth acids not being quantitative, the titania is recovered from the filtrate and the treatment repeated. The oxalate precipitates are dissolved in hydrochloric acid and the oxalic acid destroyed by permanganate; the earth acids are precipitated from the acid solution as tannin complexes. The ignited precipitates are finally submitted to tartaric hydrolysis (*v. supra*).

THE SEPARATION: Precipitation of the Major Earth-acid Fraction.—The mixed oxides (0.2 to 0.3 grm.) are brought into solution by fusion with potassium bisulphate (2 grms.) in a silica crucible and treatment of the fusion product with a hot solution of ammonium oxalate (2.0 grms.) in an 800 c.c. beaker. Five grms. of sodium salicylate B.P. are dissolved in hot water and added to the boiling solution (bulk, 250 c.c.), which is stirred and precipitated with a small excess of a 20 per cent. calcium chloride solution, added gradually in small portions. The solution must not be allowed to cool at this stage or to stand any length of time, otherwise orange crystals of the titanium compound may contaminate the oxalate precipitate. Hence, after five minutes' settling on a boiling water-bath, the clear supernatant liquid is tested for complete precipitation with a little calcium chloride solution, and filtered at once by suction on an 11 cm. Postlip filter, supported by a platinum conc. The precipitate is well washed with a hot 2 per cent. sodium salicylate solution till the washings are colourless. The hot filtrate and washings are transferred to another 800 c.c. beaker and evaporated. The oxalate precipitate is returned to the precipitation vessel; the paper is washed with hot water, then with 40 to 50 c.c. of hydrochloric acid (1:1), and discarded. The hydrochloric solution is boiled, the precipitate readily dissolving, and cautiously treated with excess of strong permanganate solution. When the transient brown colour of the higher manganese compounds has been discharged by further boiling, the liquid is diluted to 300 or 350 c.c. with boiling water, treated with one grm. of tannin in strong, freshly-made solution, boiled for another ten minutes, and the precipitate

left to settle completely on the water-bath. The above manipulations occupy two hours or less. The precipitate, TP^1 , is collected on a loose filter, washed with 2 per cent. ammonium chloride solution containing a little tannin, and ignited wet in a porcelain crucible.

Precipitation of the Minor Earth-acid Fraction.—When the bulk of the orange salicylic filtrate has been reduced to about 150 c.c., the hot liquid is treated with pure, solid ammonium chloride (about 40 grms.) until a copious yellow crystalline precipitate forms, and left to itself overnight. A large part of the coloured titanium compound crystallises out during evaporation, but the addition of ammonium chloride (an observation made and placed at our disposal by our collaborator, Mr. A. R. Powell) depresses its solubility so much that the titania is almost wholly precipitated. The crystals are filtered off by suction and washed with saturated ammonium chloride solution; they are returned to the beaker, which is set aside after the filter has been washed with hot water and discarded.

The mother liquor from the salicylate crystals is boiled with 5 grms. of ammonium acetate and 0.5 gm. of tannin till the small precipitate flocculates. This is filtered off, washed with 2 per cent. ammonium chloride-tannin solution, ignited wet, and fused with a very little bisulphate. The product is dissolved in a hot solution of ammonium oxalate (2.0 grms.), and the liquid rinsed into the beaker containing the yellow titanium crystals. On being heated, they readily dissolve, leaving a white residue of calcium oxalate, which is not filtered off. Sodium salicylate (5 grms.) is now added, the volume made up to 250 c.c., and the boiling liquid precipitated with calcium chloride, etc., exactly as before: the final product is the ignited tannin precipitate TP^2 .

The second salicylate filtrate and washings should be perfectly clear; any turbidity is filtered off, washed, and added to the oxalate precipitate.

Treatment of the Tannin Precipitates.—The precipitate TP^1 is fused with bisulphate (0.25 gm.) for tartaric hydrolysis. The tartaric solution, before precipitation with nitric acid, is filtered through a small filter for the elimination of any insoluble (siliceous) particles. The washed filter is incinerated and the ash added to the ignited precipitate TP^2 , which is evaporated in a tiny platinum cup (made of foil) with one drop of sulphuric and a little hydrofluoric acid. The dry residue is fused with a small particle of bisulphate, dissolved in about one c.c. of tartaric acid solution, and the clear liquid added to the solution of TP^1 . This is boiled in suitable bulk (TP^1 may be weighed as a guide) with nitric acid, etc., as described before. The precipitate, HP , is ignited and weighed, and finally tested colorimetrically for titania, which is often entirely absent; $(HP - TiO_2) = (Ta, Nb)_2O_5$.

RESULTS OF TEST ANALYSES.—In the table below we give the results of ten consecutive test analyses of mixtures the M_2O_5 content of which (with the exception of Nos. 9 and 10) was unknown to the operator. In Exps. 9 to 12 the minor fraction was not recovered; in the six subsequent tests we weighed the major and

minor fractions separately (HP^1 and HP^2), so as to furnish data for a critical discussion of the method.

Exp.	M_2O_5 taken.	TiO_2 added.	HP^1 .	HP^2 .	TiO_2 in HP .	M_2O_5 found.	M_2O_5 error:	
	Grm.	Grm.			Grm.	Grm.	observed.	corrected. ³
Ta9	0.0148	0.2036	0.0126	—	0.0005	0.0121	—0.0027	—0.0002
Nb10	0.0159	0.2024	0.0135	—	0.0002	0.0133	—0.0026	—0.0001
Ta11	0.0116	0.2000	0.0089	—	nil	0.0089	—0.0027	—0.0002
Nb12	0.0104	0.2006	0.0069 ¹	—	nil	0.0069	—0.0035 ¹	—0.0010 ¹
Ta13	0.0128	0.2040	0.0096	0.0005	nil	0.0101	—0.0027	—0.0002
Nb14	0.0150	0.2004	0.0118	—	trace	0.0118	—0.0032	—0.0007
EA15	0.0338	0.1500	0.0291	0.0008	0.0001	0.0298	—0.0040	—0.0005
„ 16	0.0065	0.2513	0.0052	nil	nil	0.0052	—0.0013	+0.0002
„ 17	0.0240	0.2026	0.0209	0.0006	0.0005 ²	0.0210	—0.0030	0.0000
„ 18	0.0034	0.2506	0.0016	0.0004	nil	0.0020	—0.0014	+0.0001

¹ Filtrate from oxalate precipitate slightly cloudy: low result.

² TiO_2 co-precipitated in tartaric hydrolysis because solution was too concentrated (*v. supra*).

³ For correction factor, see below.

At first sight the observed errors may appear sufficiently high to excite adverse comment; but we would remind our critics that we are at grips with a problem of such complexity as to have defeated the efforts of its ablest investigators, so that an alternative method is not yet available (see Sections IX, *loc. cit.*, and XII, ANALYST, 1928, 470). That being understood, we may explain that the error can be reduced to very small proportions by the application of an empirical correction factor, an expedient recognised as legitimate even in much simpler cases. Now the observed errors are consistently negative. We ascribe them to incomplete earth-acid flocculation at the calcium oxalate precipitation stage, the amount remaining in colloidal suspension being determined to a greater extent by the volume of solution than by the absolute quantity of earth acid present: the figures show that the loss does not increase proportionally with the weight taken, the absolute error being low but the relative error high in the case of small quantities (Exps. 16, 18), and *vice versa* (Exps. 15, 17). We propose the following corrections:

M_2O_5 found,	<0.0060 grm.:	add 0.0015 grm.
	0.0060 to 0.0100 grm.	0.0020
	0.0100 „ 0.0160	0.0025
	0.0160 „ 0.0260	0.0030
„ „	>0.0260 grm.:	„ 0.0035 „

When these are applied, we get within the limits of experimental error (see table), Exp. 12 being disregarded as not having proceeded smoothly. For the present we confine the application of the method to a maximum quantity of 0.04 grm. M_2O_5 . For larger quantities the tartaric hydrolysis method is available: this is followed up by the present procedure applied to the titania fraction, so that, in all cases, the final earth-acid error is limited to that incurred and allowed for in the oxalate-salicylate method. Its chief merit is, that it furnishes an earth-acid product so low in titania that it permits of the subsequent separation of tantalum from niobium by tannin (Section XI, ANALYST, 1928, 265). There is

no appreciable difference in the behaviour of tantalum and niobium in the oxalate-salicylate method (Exps. 9 to 14), hence the earth-acid correction is apportioned between the two elements according to the ratio ascertained by the tannin method.

Only one more observation is needful, namely, some comment on the poor earth-acid recovery in HP^2 , as compared to the amount not precipitated in HP^1 . Thus, in Exp. 15, the recovery of 0.0008 grm. HP^2 from 0.0047 grm. is disappointing, seeing that Exp. 18 yielded 0.0016 grm. HP^1 , out of 0.0034 grm. taken. So far we are at a loss for an adequate explanation, but hope to return to the matter in due course as we are continuing our researches. These have, as their next object, the full quantitative separation of tantalum, niobium, and titanium in various proportions by a combination of the published methods.

In the tartaric hydrolysis process the same cause of error (incomplete flocculation) operates as in the oxalate-salicylate method: for "all the net earth-acid results show a negative error" when the operation is carried out in a bulk of 300 c.c. (Section IX); on the other hand, the error is inappreciable in small volumes of solution (this Section).

We have not investigated the composition of the salicylic titanium complex formed in our separation process, beyond ascertaining that it is not simply titanium salicylate, but the sodium salt of a complex titanylsalicylic acid. It crystallises in glittering orange oblique prisms soluble in water or alcohol; the salt appears capable of reacting with the excess calcium chloride, part of the sodium being replaced by calcium. The exact constitution of the compound is of less analytical importance than the fact that this is another instance of a fairly successful separation procedure based on the formation of a stable crystalloidal compound, in accordance with the principles laid down in the preamble to Section VI (ANALYST, 1926, 51, 613).

UNSUCCESSFUL SEPARATION SCHEMES.—We think it useful to record as briefly as possible, without numerical data, the schemes which, in our hands, proved abortive.

A. Employing Salicylic Acid.—(1) On further investigation, procedure E, Section IX, Part I (*loc. cit.*)—salicylate extraction of a mixed ammonia precipitate—did not lead to an improved separation.—(2) The salicylate method of Dittrich and Freund for the separation of titanium from zirconium (*Z. anorg. Chem.*, 1907, 56, 344) was applied, but unsuccessfully, to the recovery of small quantities of earth acids in admixture with much titania.—(3) We vainly attempted a separation by endeavouring to take advantage of the solubility of the salicylic titanium complex in alcohol.

B. Employing other Reagents.—(1) Pyrocatechol: we confirmed the observation of Rosenheim and Sorge (*Ber.*, 1920, 53, 937) that precipitated titanous acid is directly soluble in a boiling ammoniacal pyrocatechol solution, but were unable to utilise this remarkable reaction for separation purposes.—(2) Sodium peroxide:

we were led to experiment with the metallic per-acids, in alkaline as well as in acid solution, but without any success.—(3) Precipitation of sodium tantalate and niobate from tartrate solution: like the separation of tungsten from the earth acids (Sect. VIII, ANALYST, 1927, **52**, 511), this scheme is based on the insolubility of sodium tantalate and niobate. After fusion of the oxides with potassium carbonate and solution in tartaric and a little nitric acid, the liquid was treated with sodium hydroxide and solid sodium nitrate. The earth acids were precipitated as crystalline sodium salts fairly free from titania, but the precipitation was far from quantitative and had to be completed by boiling with an excess of nitric acid: hence this procedure is more complicated and less effective than direct tartaric hydrolysis.—(4) Citric hydrolysis: the operations are exactly the same as in tartaric hydrolysis, but citric is used instead of tartaric acid. This gave very incomplete earth-acid precipitation, as the citric complexes have greater stability than those of other organic hydroxy-compounds. Here again, tartaric hydrolysis is the better method.

SUMMARY.—A new method is described for the separation of small quantities of earth acids from large amounts of titania. The solution, containing the oxalates of titanium and ammonium and the oxalo-earth acids, is treated with sodium salicylate, whereby the titania becomes converted into a stable crystalloidal sodium titanylsalicylate. The hot solution is then precipitated with calcium chloride, the bulky precipitate carrying down the earth acids. They are recovered by solution of the precipitate in hydrochloric acid, destruction of the oxalic acid with permanganate, and precipitation with tannin. The tannin precipitate is purified by fusion with bisulphate, solution in tartaric acid, and boiling with excess of nitric acid in very small bulk. The soluble titania fraction is again submitted to the above procedure, after having been precipitated by evaporation and saturation with ammonium chloride of the filtrate from the oxalate precipitate. The errors are consistently negative, a few mgrms. of earth acid escaping precipitation; but serviceable results are secured by the application of an empirical correction. The final pentoxide precipitate is free, or practically free, from titania.

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Potassium Cyanate as a Reagent for the Detection of Cobalt.

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(Read at the Meeting, April 3, 1929.)

AMMONIUM thiocyanate has long been used as a reagent for the detection of cobalt in the presence of nickel (Vogel, *Ber.*, 1879, 12, 2314; Treadwell, *Z. anorg. Chem.*, 1901, 26, 105; see also Treadwell and Hall, *Analytical Chemistry*, Vol. I, 4th ed., pp. 182-3; p. 184). Complications arise if iron is present, due to the intense blood-red colour of ferric thiocyanate. These difficulties may in some measure be overcome if concentrated ammonium acetate and tartaric acid solutions are added to prevent the formation of coloured iron derivatives, or the iron may be removed by the addition of sodium carbonate solution, or of sodium thiosulphate.

The use of potassium cyanate, instead of potassium or ammonium thiocyanates, seems never to have been suggested, although the cyanate appears to present marked advantages over the thiocyanate method. Iron and nickel do not give coloured complexes with this reagent, whilst the deep blue colour of the cobalt complex formed with potassium cyanate is quite as intense as that obtained with ammonium thiocyanate.

The test was carried out in all cases by adding measured volumes of aqueous solutions of cobalt nitrate (iron and nickel free) to 2 c.c. of an alcoholic solution of potassium cyanate (prepared by shaking sufficient potassium cyanate with absolute alcohol at room temperature so that some of the solid remained undissolved; the filtered solution thus prepared contained 3.8 grm. of potassium cyanate per litre). This procedure is much more convenient to carry out than the shaking of the aqueous solution with amyl alcohol and ether, as in the ammonium thiocyanate test. The following table shows the results of adding volumes of molar cobalt nitrate solution (column one) to 2 c.c. of the alcoholic solution of potassium cyanate :

Vol. added. c.c.	Colour.
0.3	Deep royal blue, with reddish tinge.
0.2	" " " " "
0.1	Deep royal blue
0.05	diminishing
0.04	in
0.02	intensity.
0.01	Pale blue.

A precipitate was present in each case in diminishing quantity (probably potassium nitrate). The reddish tinge in the first two cases is doubtless due to the cobalt nitrate being present in excess. No change took place on allowing the solutions

to stand overnight, except that the reddish tinge in the first case appeared more marked. These experiments were repeated with tenth molar and one-hundredth molar cobalt nitrate solutions; but even with 0.01 c.c. of one-hundredth molar cobalt nitrate solution, corresponding to 6×10^{-6} grm. of cobalt ion, a very pale blue colour was obtained, which was none the less quite definite. The test is much more delicate when carried out as above than when made in aqueous solution. The gradual addition of water to the solutions containing the cobalt complex in the above tests caused the blue colour to weaken, and in each case the addition of 3-4 c.c. of water destroyed it. (Cf. Schneider, *Ber.*, 1895, 38, 1540, who used cobalt acetate, added to an alcoholic solution containing potassium cyanate, as a test for cyanate in the presence of cyanide.)

INFLUENCE OF NICKEL.—With molar nickel sulphate solution (free from iron and cobalt) the addition of diminishing quantities of this solution (0.3 c.c. \rightarrow 0.01 c.c.) to 2 c.c. of alcoholic potassium cyanate caused a pale green precipitate to form immediately in diminishing quantity, as the series descended. The supernatant liquid was colourless. Similar results were obtained when tenth molar nickel sulphate solution was used. The results for mixed cobalt and nickel solutions are given below:

	c.c.		
$M/20 \text{ Co}(\text{NO}_3)_2 + M/20 \text{ NiSO}_4$	0.04	Distinct blue colour.) Precipitates as described in following set.
	0.02	" " " "	
	0.01	Pale " blue " colour."	
$M/40 \text{ Co}(\text{NO}_3)_2 + M/40 \text{ NiSO}_4$	Volumes added 0.3 c.c. \rightarrow 0.01 c.c.		

The colour of the first solution (0.3 c.c.) was deep blue, and a greenish-white flocculent precipitate formed immediately. The intensity of the colour, also the amount of the precipitate, diminished as the series was passed down, but the colour was quite pronounced in the last tube. The addition of 0.1 c.c. of $M/200 \text{ Co}(\text{NO}_3)_2 + M/2 \text{ NiSO}_4$ caused a definite blue-green colour, and the colour persisted in the filtered solution. As little as 0.3 mgrm. of cobalt ion may thus be detected in the presence of one hundred times as much nickel ion. The presence of still greater relative amounts of nickel does not invalidate the test, as shown by the following experiment:—A tenth of 1 c.c. of a warm solution of 5M nickel sulphate and $M/200$ cobalt nitrate was added to 8 c.c. of the cyanate reagent. A greenish-white precipitate rapidly settled, and the solution was then concentrated to half its bulk by boiling, and filtered. A little solid potassium cyanate was added to the filtrate, which was then concentrated to approximately 2 c.c., and filtered. A clear blue solution was obtained. A blank experiment with nickel sulphate alone gave a colourless, but slightly turbid, solution. One part of cobalt in the presence of one thousand parts of nickel was thus detected.

The test can accordingly be applied for the detection of cobalt in the presence of nickel in the usual scheme of qualitative analysis by adding ammonia to the solution obtained after dissolving the mixed cobalt and nickel sulphides until the solution is faintly alkaline, and then adding one drop of this solution to 2 c.c. of

alcoholic potassium cyanate solution. A blue coloration, resembling cuprammonium solutions in appearance, shows the presence of cobalt.

INFLUENCE OF FERRIC IRON.—The results were as follows for ferric chloride solution ($M/2$):

Vol. added. c.c.	RESULT.	
	At once.	After standing overnight.
0.3	Clear orange-brown solution.	No change.
0.1	Turbid orange-brown solution.	Precipitate settled.
0.05	More turbid orange-brown solution.	" "
0.02	Turbid light brown solution.	Precipitate settled and solution almost colourless.

Iron was, however, completely removed from solution as follows:—0.1 c.c. of $M/2$ ferric chloride was added to 2 c.c. of alcoholic potassium cyanate, and the solution was boiled and filtered. A small amount of iron remained in solution. A further 2 c.c. of cyanate were added, and the liquid re-boiled and filtered, when a colourless solution was obtained. With $M/10$ ferric chloride solution, added in the same quantities as above, the immediate colour effects and precipitations were as above, but were less pronounced; precipitation was practically complete in each case after standing overnight. With $M/100$ ferric chloride solution, the solutions varied from pale brown to colourless (for 0.02 c.c. of solution). The colour of the alcoholic solution of potassium cyanate after adding the ferric chloride solution was a slightly deeper brown than that of the aqueous ferric chloride used. After standing overnight the solutions which were filtered from the brown precipitates were colourless. The results for a solution containing $M/10$ ferric chloride and $M/10$ cobalt nitrate are given below :

Vol. added. c.c.	Immediate result.
0.3	Brownish-green solution.
0.2	Olive-green solution.
0.1	Blue-green solution; intensity of colour diminishing, but still quite definite in the last solution.
0.05	
0.03	
0.02	
0.01	

After standing overnight the ferric salt had precipitated completely in each tube, leaving a blue solution, the depth of the colour diminishing as the series was passed down. Thus, although the brown colour due to the ferric salt masks the blue colour of the cobalt complex to some extent, the colour change is none the less quite definite and distinctive, and is even more decisive if the solutions are allowed to stand. Experiments with $M/2$ ferric chloride and $M/200$ cobalt nitrate solution gave a conclusive test for cobalt as follows:—

On adding 0.1 c.c. of the solution to 2 c.c. of cyanate reagent an orange-brown solution was obtained. Boiling and filtering removed most of the iron, but the solution was still orange-brown. A further 2 c.c. of cyanate were added, the

solution re-boiled and filtered, when a pale blue-green solution resulted. Similar treatment of ferric chloride alone (see above) gave a colourless solution. The presence of one part of cobalt in 100 parts of iron was thus detected, but this does not represent by any means the limit of the relative amounts of iron and cobalt, for the presence of one part of cobalt in the presence of 1600 parts of iron was shown quite definitely as follows:—

An addition of 0.1 c.c. of a solution of 8 *M* ferric chloride and *M*/200 cobalt nitrate was made to 8 c.c. of cyanate reagent. A reddish-brown precipitate at once separated, and the solution was then boiled and filtered with the aid of the pump, a few crystals of potassium cyanate added, the solution reboiled and concentrated to about half bulk, and again filtered, when a greenish-brown solution resulted. Further crystals of potassium cyanate were added, the solution concentrated by boiling to about 2 c.c., when a pale blue-green solution resulted, showing the presence of cobalt. A blank experiment was carried out as described above, 0.1 c.c. of 8 *M* ferric chloride solution being used, when a colourless solution showing no trace of blue-green colour resulted. Some cobalt was doubtless removed during the elimination of iron from solution, for the colour of the resulting solution was not so deep as for 0.1 c.c. of *M*/200 cobalt nitrate solution alone.

REACTIONS WITH OTHER METALS.—Experiments were carried out on the addition of all the common cations (1 drop of 2*N* solution) to 2 c.c. of alcoholic potassium cyanate reagent. Only in the cases of ferric and of copper salts were coloured solutions obtained. Detailed experiments showed that a blue coloration, due presumably to the cupric ion, results on adding cupric salt solutions to the cyanate, but all the copper is precipitated on standing, a colourless solution being obtained. Experiments were made with mixed cobalt and copper solutions; and, although the colour of the cobalt complex was obtained after the liquid had stood sufficiently long for all the copper salt to be precipitated, a better method of procedure would be to remove the copper in acid solution by means of hydrogen sulphide, boil off the excess of hydrogen sulphide, and then add one drop of the solution remaining to 2 c.c. of the cyanate reagent. In this way 0.01 c.c. of a solution containing *M*/2 CuSO_4 and *M*/2 $\text{Co}(\text{NO}_3)_2$ gave a deep blue coloration with the cyanate reagent, whilst 0.09 c.c. of *M*/2 CuSO_4 and *M*/200 $\text{Co}(\text{NO}_3)_2$ gave a perfectly definite test for cobalt.

Coloured solutions or precipitates were also obtained on adding the following solutions to the cyanate reagent in the usual way:—

- Uranium acetate: Yellow solution and almost immediate separation of pale yellow precipitate.
- Titanous chloride: Purple turbidity, completely precipitated on standing a short time.
- Gold chloride: Lemon yellow solution, no precipitate.
- Vanadium sulphate: Deep greenish brown flocculent precipitate.

In the case of vanadium sulphate it would appear that a vanadium complex is precipitated, since the addition of vanadium sulphate solution to alcohol alone

gives only a very slight precipitate and a brown coloured solution. A blue coloration is also obtained by adding two drops of ammonium molybdate to 2 c.c. of potassium cyanate reagent to which one drop of reagent solution of stannous chloride has been added. It seems unlikely, however, that such a combination of circumstances would arise to cause complication in carrying out the cobalt test. Tungsten has a similar effect.

PREPARATION OF THE COBALT COMPLEX.—The blue complex formed by cobaltous salts with potassium cyanate was prepared by Blomstrand (*J. prakt. Chem.*, 1871, [2], 3, 221) by dissolving cobaltous oxide in glacial acetic acid and adding potassium cyanate, presumably using concentrated solutions. A deep blue crystalline solid separated on allowing the solution to stand overnight (Blomstrand found $K=25.86$, $Co=19.34$ per cent.; $K_2Co(CNO)_4$ requires $K=25.57$, $Co=19.35$ per cent.). Blomstrand's method of preparation was repeated; a crop of crystals was rapidly separated by cooling the mixed solutions in an ice-salt freezing mixture; these were filtered with the aid of the pump, dissolved in a small quantity of cold water, cooled in the freezing mixture, and the crop of crystals, which separated at once, filtered off and air-dried. The crystals retained a very slight smell of acetic acid, and were therefore purified by dissolving in acetone, followed by precipitation by means of ether.

ANALYSES.—A quantity of 0.2028 grm. of substance gave 0.21 grm. of $CoSO_4 + K_2SO_4$ (by Main Smith's method, *J. Soc. Chem. Ind.*, 1925, 44, 539T; *Chem. News*, 1926, 132, 65), whence $Co+K=44.55$ per cent.; calc. for $K_2Co(CNO)_4$, $Co+K=44.92$ per cent. Nitrogen was determined by Kjeldahl's method (Found 17.8, 18.0 per cent.; calc. 18.36 per cent.) Several determinations of carbon were carried out by decomposing the complex with dilute sulphuric acid, and by weighing the carbon dioxide evolved. The results in all cases were low (found, for example, $C=13.47$, 12.93, 14.59 per cent.; calc., $C=15.74$ per cent.). It therefore seems certain that the complex does not undergo complete conversion into carbonate when decomposed in this way, and that other substances, possibly urea, are formed (cf. O. and I. Masson, *Z. physikal. Chem.*, 1910, 70, 290, who consider that potassium cyanate decomposes in aqueous solution in accordance with the equation $4KCNO + 6H_2O \rightarrow 2K_2CO_3 + (NH_4)_2CO_3 + CO(NH_2)_2$).

PREPARATION OF POTASSIUM COBALTOCYANATE.—The preparation of potassium cobaltocyanate was also carried out by mixing solutions of potassium cyanate (30 grms. in 40 c.c. of water) and cobaltous sulphate (30 grms. in 40 c.c. of water) at room temperature. A very deep blue solution was obtained, and a precipitate (12.5 grms.) separated at once, whilst a further 2.5 grms. deposited after standing a short time. These crops probably are mainly potassium sulphate. Deep blue crops were obtained by the addition first of alcohol and then of ether to the solution remaining (total weight of product 24 grms.). Analyses of these crops gave variable results, but purification by extraction with acetone, followed by precipitation with ether, yielded pure potassium cobaltocyanate (found $Co+K=44.69$ per cent.).

DISCUSSION.

The PRESIDENT congratulated the authors on discovering, or, at any rate, adapting, a delicate and distinctive test for cobalt. With regard to the use of alcohols, since water was so destructive to the delicacy of the test, he would like to enquire whether the small amount of water in industrial methylated spirit would be destructive. Secondly, he would like to know what was the nature of the solution applied; was it a neutral solution?

Dr. DUNN suggested that, as the colour was so clear in this test, it might be possible not only to detect but also to determine cobalt in this way. He congratulated the authors on the clearness with which the test was described.

Dr. WARD, replying, stated that he and his co-worker had not tried the test with industrial methylated spirit, but he thought that the small amount of water present would not decrease the sensitiveness of the test or prevent its being carried out satisfactorily. With regard to the solution used, there was no need to take any special precautions, beyond using the salts dissolved in water. He had made no attempt to put this test on a quantitative footing, but it seemed quite feasible that this might be done.

Official Appointments.

Mr. F. C. BULLOCK, B.Sc., F.I.C., as Public Analyst for the County Borough of Leicester (to date from July 1st, 1929).

Mr. ERIC VOELCKER, A.R.C.S., F.I.C., as Additional Public Analyst for the County of Northampton (June 7th, 1929).

Notes.

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

RICE HUSKS IN BRAN AND SHARPS.

A SAMPLE of bran and a sample of sharps examined by the writer a few months ago were both found to be adulterated with rice husks.

Although a prosecution arising from the presence of rice husks in sharps is on record (ANALYST, 1924, 49, 429), the use of this substance as an adulterant of bran and sharps is not, to the knowledge of the writer, a common practice.

It seemed, however, that the present note might prove useful, in view of the fact that, since the Fertilisers and Feeding Stuffs' Act (1926) became operative, the number of samples of mill offals submitted for analysis has increased considerably.

Rice husks are light brown in colour; the outer surfaces have a dull appearance, whilst the inner surfaces are shiny. They are very stiff and hard, and are characterised by their rough, harsh nature. This harshness is easily detected by scraping the outer surface with a needle.

In bran, the particles of rice husk may be large enough for them to be recognised by the above characteristics; but in sharps, where the particles are much smaller, their detection by the naked eye is usually impossible.

Samples of bran or sharps, which contain a considerable proportion of rice husks, will indicate this adulteration in their fibre content; whereas a normal bran has a fibre content of 7 to 10 per cent., and a normal sharps of 4.5 to 6.5 per cent., rice husks contain about 40 per cent. of fibre. It must be remembered, however, that it is possible to obtain samples of sharps with a fibre content of about 3.5 per cent., and such samples, even after an adulteration with 10 per cent. rice husks, would have a fibre content within the normal range.

The structure of the rice husk is so different, however, from that of the wheat grain, that the detection of rice husk in bran and sharps by microscopical examination is a simple matter.

A little of the suspected sample of bran or sharps is boiled with a solution of chloral hydrate (water 2, chloral hydrate 5 parts), and a drop of the liquid is then placed on a microscope slide, covered with a coverslip, and examined.

Rice husks, which are the glumes and paleae of the fruit, consist of four layers of tissue, *viz.* outer epidermis, fibrous hypodermis, spongy parenchyma, and inner epidermis. It is by the cells of the outer epidermis, which are very characteristic, that the particles of rice husk are recognised. These cells (see Fig.), which are arranged in longitudinal rows, are square in general outline, but their side walls are extremely sinuous. This peculiar sinuous form is very distinctive. The epidermis also bears dagger-shaped hairs, and in places, where these have become detached, hair scars can be seen.



Although rice husks, owing to their high silica content, do not yield to clearing treatment for microscopical examination so readily as many seed tissues, they can be resolved into their elements by maceration in Schulze's fluid. This treatment is not necessary for their identification, however, since the outer epidermal cells with the characteristic sinuous form are easily rendered visible by boiling with chloral hydrate solution. (*Cf.* Schröder, *ANALYST*, 1908, 33, 280; Silberberg, *Id.*, 1923, 48, 186; *A.O.A.C. Methods*, 1925, p. 122.)

A. J. AMOS.

MESSRS. WOODLANDS LTD.,
CHARLTON GREEN, DOVER, KENT.

A NEW SENSITIVE COLOUR REACTION OF COPPER.*

CERTAIN oxidising agents, when added to very dilute feebly alkaline solutions of a cupric salt containing dimethylglyoxime, produce an intense reddish-violet colour resembling that of permanganate. That produced by sodium hypochlorite or bromine water is rather fugitive, partly due to the sensitiveness of the colour to acid and excess alkali, and to the difficulties of adjusting the P_H value when using these oxidants. Ammonium persulphate produces a weak reddish colour, but on addition of a trace of silver nitrate, an immediate development of the intense permanganate colour occurs, especially when pyridine is used as the means of obtaining slight alkalinity. As a result of many experiments carried out to determine the concentration of reagents most favourable for the reaction, the following

* Communication from the Research Department, Woolwich.

is proposed as a method for the detection and determination of traces of copper in solution:—

The solution, which must be free from chloride, is neutralised and rendered very faintly acid (1 drop of dilute (1:3) sulphuric acid in excess). It is placed in a 100 c.c. Nessler glass, made up to volume, and 1 gm. of ammonium persulphate is dissolved in the solution; 1 c.c. of saturated alcoholic dimethylglyoxime, 0.5 c.c. of a 0.5 per cent. solution of silver nitrate, and 2 c.c. of 10 per cent. aqueous pyridine are added, and the whole is stirred. The colour may be compared colorimetrically by running a standard solution of copper sulphate (1 c.c. = 0.00001 gm. of Cu) into 100 c.c. of a solution containing the same amounts of reagents. The comparison should be carried out without undue delay, as the colour shows some tendency to fade on standing. Where slight opalescence, due to traces of chloride (impurity in the reagents) appears, it is permissible to discharge it by adding a little more than the specified amount of pyridine. As little as 0.01 mgrm. of copper yields a distinct reddish-violet colour, the method is not suitable for determining more than 0.1 mgrm. One part of copper can be readily detected in 10,000,000 parts of water. Comparative tests at 100 c.c. volume with the xanthate and ferrocyanide methods have shown that this reaction is somewhat more sensitive than the former, and from five to ten times as sensitive as the latter. Small amounts of certain other heavy metals give yellowish or brown colorations under the conditions of the test, but the reddish-violet colour appears to be specific for copper.

S. G. CLARKE.

B. JONES.

MEASUREMENT OF THE STRENGTH OF SUNLIGHT.

THE note by H. H. Bagnall (ANALYST, 1929, 101) is an interesting and valuable practical contribution to the study of the comparison of the ultra-violet radiations reaching town and countryside. Whilst we believe that the figures give an indication of the quantities of ultra-violet radiation present at the various places, and also that the conclusions drawn are sound, yet it appears to us that the method is open to some theoretical criticism.

(1) The reactions should be conducted in quartz and not in glass vessels. Ordinary window glass (2 mm. thick) absorbs all radiations shorter than $320\text{ }\mu\mu$, and bottle glass probably absorbs still more of the ultra-violet spectrum. This means that the range $295\text{ }\mu\mu$ to $320\text{ }\mu\mu$ present in brilliant summer sunlight does not reach the test solution, and it is the radiations within this range that produce many of the most beneficial therapeutic and bactericidal effects. Hence the ratio of effective ultra-violet radiation at, say, Regent Road and Nab Top Sanatorium, may be very different from that indicated by the ratio 744.5:885.8. The wave-lengths shorter than $320\text{ }\mu\mu$, probably only present at the Sanatorium, never reach the solution, and hence are not detected by the test. We also suggest the use of a spherical vessel, thereby eliminating the irregular effect of the stopper.

(2) It should be known exactly which wave-lengths accomplish the decomposition of the potassium iodide. We ourselves have used for the examination of mercury-vapour lamps a solution of uranium acetate and oxalic acid in water (*J. Soc. Chem. Ind.*, 1925, 44, 453T; *British J. Actinotherapy*, 1927, January and May), which is sensitive to ultra-violet radiation shorter than $320\text{ }\mu\mu$. Such information considerably increases the value of any actinometer test.

(3) The colour of the potassium iodide solution becomes orange as the iodine is liberated. We question whether one unit of ultra-violet radiation will liberate the same quantity of iodine from the nearly colourless potassium iodide solution

as it will liberate from an orange-coloured mixture of solutions of iodine and potassium iodide. If it does not, then the quantity of iodine liberated is not directly proportional to the amount of ultra-violet radiation incident on the solution.

J. EWART MOSS.
ARTHUR W. KNAPP.

BOURNVILLE, BIRMINGHAM.

THE DETECTION OF THE PROHIBITED VEGETABLE AND COAL TAR COLOURS IN FOODSTUFFS.

Two of the supplementary tests, as described in *THE ANALYST*, 1927, 52, 587, have been found to be unsatisfactory.

Test 16 is fallacious. The violet colour stated to be given by naphthol yellow is not due to that dye. It is given by any alkaline solution which has been shaken with ether and from which the ether has not been completely removed by boiling. The original tests were carried out on alkaline extracts obtained as detailed in the scheme on page 589. The solutions were all boiled to remove ether, but in the case of the naphthol yellow solution the removal must have been incomplete. Test 16 should be deleted.

Test 17 has been found to give a green fluorescence in certain instances with the reagents alone. This has been traced to the excess permanganate oxidising part of the resorcinol, possibly to a dibasic aliphatic acid, which then combines with the remaining resorcinol to form a fluorescing substance. In order to avoid this possibility it is necessary to reduce the excess permanganate after the oxidation. The test has therefore been modified and has been made more delicate as follows:

"To 1 vol. of the alkaline solution add $\frac{1}{2}$ vol. of concentrated sulphuric acid and a little solid permanganate. Boil for 1 minute and then decolorise the solution by the addition, drop by drop, of sodium sulphite solution. Add a few crystals of resorcinol and boil gently until the water has evaporated and fuming starts. Pour into water and extract once with ether. Wash the separated ether with water, discarding the latter, and then shake the ether with a little dilute ammonia solution." Naphthol yellow is the only one of the prohibited colours which gives a green fluorescing colour in the lower layer.

J. R. NICHOLLS.

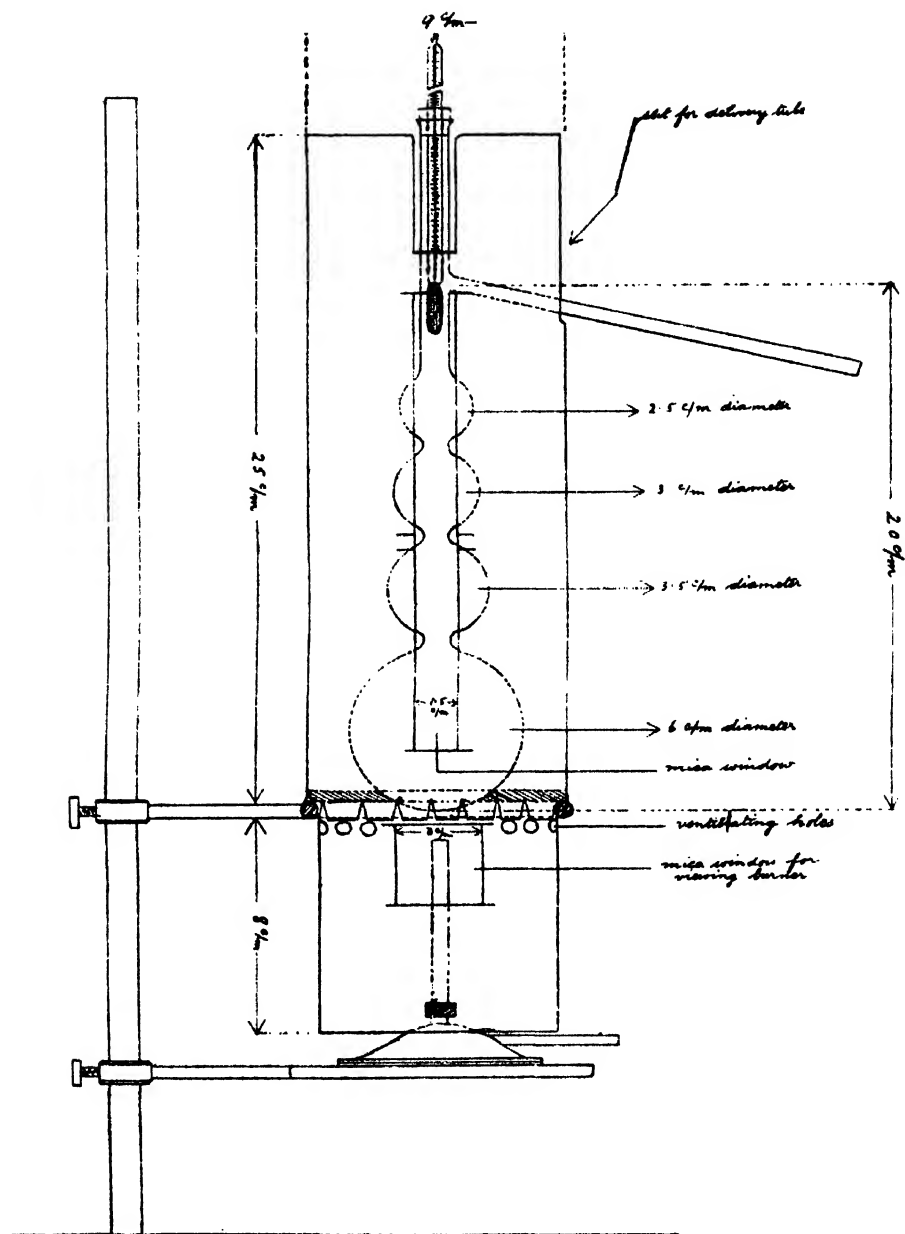
GOVERNMENT LABORATORY, W.C.2.

Report of the Essential Oil Sub-Committee to the Standing Committee on Uniformity of Analytical Methods.

• PHYSICAL CONSTANTS (2).

THE Sub-Committee make the following recommendations:—

FREEZING AND MELTING POINTS.—The apparatus recommended consists of a stout-walled glass test tube, 125 mm. \times 30 mm. (inside measurements), fitted into a wide-mouthed jar or bottle of about 500 c.c. capacity, by means of a bored cork; and an inner test tube, 100 mm. \times 21 mm., fitted into the larger tube also by means



*Standard Distillation Apparatus
for Essential Oils.*

of a bored cork. The thermometer used should be readable to $1/5$ th of a degree, and should have a diameter about 5 mm. or 6 mm., and the length of the bulb should be between 15 mm. and 20 mm.

Freezing Points: Method of Procedure.—In order to obtain a preliminary indication, a few c.c. of the oil are cooled in a small test tube and stirred with the thermometer until solidification takes place; the temperature is noted and the tube of solidified oil set aside in a cool place. The outer container of the apparatus is then filled with water (or brine) at a temperature about 5 degrees lower than that indicated above, and the larger outer tube fitted in its place. Into the inner tube 10 c.c. of the oil are placed, the thermometer inserted, and the tube and oil cooled to the temperature indicated in the preliminary test. The tube and contents are now inserted in the apparatus, and the temperature allowed to fall a further 1 or 2 degrees. The oil is then seeded with a trace of the previously solidified oil and stirred with the thermometer until solidification takes place.

The highest temperature reached is taken as the freezing point.

Melting Points.—After the determination of the freezing point the inner and outer tubes are removed together from the water jacket and the temperature allowed to rise slowly, the oil being stirred continuously with the thermometer until the liquid becomes "clear." If necessary, the temperature may be raised by holding the outer tube in the hand, or, in the case of a low melting point, the water jacket may be used to prevent too rapid a rise in temperature. The temperature at which the liquid becomes "clear" is taken as the melting point.

A few crystals usually remain unmelted at this point, and the appearance of these crystals furnishes a sharp indication of the melting point. Until the liquid becomes "clear" the unmelted crystals are dull, but at the "clearing" point they suddenly become glistening.

When testing oils of low melting point, the result may be vitiated by the presence of moisture, which will prevent the "clearing" of the oil. An oil which is originally clear below its melting point may become cloudy from atmospheric moisture condensed in the tube during the cooling. In such cases the oils must be dried with anhydrous sodium sulphate.

Determinations on a number of aniseed and fennel oils by members of this Sub-Committee showed variations not exceeding $\pm 0.2^{\circ}$ C.

Otto of Rose.—In the case of otto of rose the freezing point cannot be determined by the standard method, as there is no definite rise in temperature on solidification. The following method is recommended in the case of this oil:—The prescribed apparatus is used, the outer container having been filled with water about 10 degrees below the freezing point, as indicated by a preliminary test. The oil is placed in the inner tube and stirred gently with the thermometer until crystals begin to separate. This point is taken as the freezing point. The temperature is allowed to fall a further 2 degrees, and then the two tubes together are removed from the water jacket. The temperature is allowed to rise slowly, stirring gently the while until the liquid becomes free from all but a few characteristic glistening crystals. This point is taken as the melting point. Tests may differ by as much as $\pm 0.5^{\circ}$ C.

BOILING POINTS.—The Sub-Committee consider that uniformity can be attained only by the use of standardised apparatus and conditions, and the following are recommended:—

(1) The shape and dimensions of the distilling flask are to be in accordance with the accompanying sketch.

(2) The flask is to be supported on a sheet of asbestos board through which a hole 4 cm. in diameter has been cut. Both flask and burner are to be protected from draughts by a screen, in accordance with the sketch.

(3) A plain glass tube, 1 to 1.2 cm. bore, and 65 cm. long, is to be used as an air condenser. The lower end is to be bent down and drawn out slightly. The condenser is to be connected with the delivery tube of the flask by means of a bored cork.

(4) The amount taken for the test is to be 50 c.c.

(5) The flask is to be heated by a naked flame, and a fragment of broken porcelain or pipe stem added to promote even ebullition.

(6) The rate of distillation is to be 50 to 70 drops per minute.

(7) The thermometer is to be either of the short-stem type or else corrected for emergent column, and the top of the bulb is to be level with the bottom side of the delivery tube.

(8) The temperature is to be corrected:—

(i) For variation in barometric pressure

$\pm 1^{\circ}\text{C. for each 20 mm. variant from 760 mm.}$

(ii) For emergent column by the formula:—

$$T = t + 0.000143 (t - t^1)N$$

where T = corrected temperature, t = observed temperature, t^1 = mean temperature of emergent column, and N = length of emergent column in scale degrees.

Thermometers.—The accuracy of the thermometers used in these determinations is to be checked by comparison with N.P.L. standard instruments.

(Signed),

John Allan (Chairman), C. T. Bennett, S. W. Bradley, E. Theodore
Brewis, L. E. Campbell, Thos. H. Durrans, T. W. Harrison, Ernest J.
Parry, C. Edward Sage, W. H. Simmons.

T. Tusting Cocking (Honorary Secretary).

April 26, 1929.

Legal Notes.

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

TINNED "THICK" CREAM.

ON May 3rd, a firm of grocers was summoned at Norwich for selling a tin of thick cream which was not of the quality demanded.

Mr. C. G. Ransome Williams, for the prosecution, said that the inspector bought a 6d. tin of thick cream, which, on analysis, was found to contain only 21.04 per cent. of milk fat, whereas it should have contained at least 35 per cent.; for commercial cream generally contained 50 per cent.

Mr. Gerald Dodson, for the defence, said that the importance of this matter lay in the fact that since the Regulations of 1926-1927 had prohibited the addition of all preservatives to cream a new industry had grown up. According to the old regulations it was recognised that cream containing 35 per cent. of milk fat might be preserved with boric acid, but these regulations referred exclusively to dairy cream. There was no legal standard for cream, and although the Ministry of Health had power to fix a standard, they had never done so, and this 35 per cent. mentioned in the certificate of the Public Analyst had never been fixed by law. It was therefore for the Court to decide whether the cream bought by the inspector was purchased to his prejudice. The Court had to perform the task which the Ministry might have done for it, and to decide what standard there should be for tinned cream, as opposed to dairy cream. In order to sterilise cream effectively it must not contain more than 25 per cent. of milk fat, and if more fat was present the article would not be merchantable.

The Magistrates dismissed the case.

ORANGE QUININE WINE.

A FIRM of druggists was summoned by the Bethnal Green Borough Council, on April 23rd, at Old Street Police Court, for selling orange quinine wine deficient in quinine to the extent of 17 per cent. and containing no orange wine.

The inspector said that when he unwrapped the bottle he saw that there was a label with the words "Orange Quinine Tonic."

The manager of the defendant company said that the cost of the quinine wine of the British Pharmacopoeia was 3s. 4d. per bottle, and that of the orange and quinine tonic 1s. 6d. per bottle. When some of his customers asked for orange quinine wine he found that they meant his tonic.

Mr. Glyn Jones submitted that, apart from anything else, the label on the bottle was sufficient, and there could be no conviction.

The Magistrate (Mr. Clarke Hall) said that it was clear that there had been a misunderstanding between the parties, and no intention on the part of the defendants to defraud. The summons would be dismissed.

A similar summons was brought against another firm of druggists, for selling orange quinine wine 17 per cent. deficient in quinine, and entirely deficient in orange wine, since it contained no alcohol.

The solicitor for the defence said that in view of the fact that orange quinine wine was not mentioned in the British Pharmacopoeia, the inspector's agent asked for something which did not exist, and the druggist had to do the best he could in the circumstances.

This summons was also dismissed.

NON-ALCOHOLIC RAISIN WINE.

ON April 23 a Bermondsey manufacturer answered an adjourned summons, at the Lambeth Police Court, of having given a false warranty to the effect that certain raisin wine supplied by him to an East Dulwich tradesman complied with the provisions of the Food and Drugs Act.

Mr. E. A. Pinchin, Public Analyst, certified that the contents of the bottle, which was labelled "British Non-Alcoholic Raisin Wine," consisted of a solution of sugar in water coloured with an aniline dye.

Mr. Fox-Andrews, for the defence, contended that if the article was of the recognised commercial standard, the fact that it contained no raisins did not constitute an offence.

Mr. E. J. Parry, F.I.C., said that the article made by the defendant was of the usual commercial standard in this country of non-alcoholic raisin wine. It was the only substance that could correctly be so described. In his analysis the Public Analyst had taken no notice of the flavouring.

Mr. Hodgson, barrister, appearing for the prosecution, said that the Public Analyst thought that there might be a trace of flavouring in the article. The real question in the case was what was expected by the public. Anyone asking for raisin wine would expect to find some raisin juice in it.

The Magistrate (Mr. Sandbach), giving judgment, said that it was agreed that all the ingredients found in British wines were present in this wine. He came to the conclusion that, from the commercial point of view, the article was what the consumer expected to get, and the summons would be dismissed.

An application for costs was refused.

The National Physical Laboratory.

REPORT FOR THE YEAR 1928.*

THE Report is on the same lines as last year (ANALYST, 1928, 53, 340-341), dealing with the work of the physics, electricity, metrology, engineering, metallurgy, aerodynamics depts., and the William Froude National Tank. A special report is included on the units and standards of measurement used at the Laboratory. This defines the units, international and British Imperial, with information as to the primary standards preserved and maintained at the Laboratory, and in a few special cases particulars of secondary standards. (For information on the proposed International Temperature Scale see ANALYST, 1929, 292.)

Physics Dept.—Work has been begun on the specific heat of gases at high temperatures and high pressures; the latent heat and specific volume of sulphur dioxide are being redetermined in order to supply more reliable data for the construction of entropy-temperature diagrams for various refrigerants; the study of the laws governing the efficiency of water sprays for moistening and cooling air has been begun, and the moisture absorbing properties of silica gel are being investigated. A number of investigations have been undertaken in the industrial applications of X-ray crystal analysis (including the examination of tungsten magnet steels and the effect of heat treatment). The selective orientation of the crystals obtained in rolling aluminium is largely influenced by the previous history of the specimen. The International unit for X-ray measurement of dosage is now agreed upon as "the quantity of X-radiation which, when the secondary electrons are fully utilised, and the wall effect of the chamber is avoided, produces, in 1 c.c. of atmospheric air at 0° C. and 76 cm. mercury pressure, such a degree of conductivity that one electrostatic unit of charge is measured at saturation current."

Metrology Department.—The preliminary work on pivots and jewels in instruments shows that rust is formed on the end of the pivot as it rotates in contact with the jewel, and does not appear when the pivot remains stationary, and increases

* Obtainable at Adastral House, Kingsway, W.C.2. Price 7s. 6d.

as the number of revolutions increase and concurrently with the torque due to friction. *Glass Volumetric Apparatus and Hydrometers*.—The Dairy Research Committee have drawn up a memorandum and questionnaire dealing with co-ordination of specifications of glassware used for testing milk and milk products which has been sent to all governments of the Empire interested. A "strain-viewer" has been made for examining colorimetric glassware, consisting of a polarising mirror on the base of a wooden box reflecting a beam of polarised light through a ground glass window in the side of the box, the apparatus in front of the window being examined through a Nicol prism on a vertical brass column. During 1928, 5099 pieces of glass-ware were tested, an increase of 50 per cent. over the previous year. A draft specification for a series of hydrometers small enough to be used with 50 ml. samples has been prepared; 645 (against 679 for 1927) hydrometers were tested during 1928.

AERODYNAMICS DEPARTMENT.—The construction of the new Compressed Air Tunnel has been begun.

METALLURGY DEPARTMENT.—A great deal of work has been done on the preparation of pure iron and chromium; the physical structure of metals and alloys, including study by means of X-rays, has continued to receive attention; a considerable number of single crystals of various metals has been produced, having diameters up to $1\frac{1}{4}$ in.; exploratory work on new alloys, particularly of those in which aluminium is the predominant metal, has been undertaken, and alloys for high temperature work have been prepared.

D. G. H.

Parliamentary Notes.

ARTIFICIAL CREAM ACT, 1929.*

AN ACT TO REGULATE THE SALE AND MANUFACTURE OF ARTIFICIAL CREAM. [10th May, 1929.]

BE it enacted by the King's most Excellent Majesty, by and with the advice and consent of the Lords Spiritual and Temporal, and Commons, in this present Parliament assembled, and by the authority of the same, as follows:—

1.—(1) No person shall sell or offer or expose for sale for human consumption under a description or designation including the word "cream" any substance purporting to be cream or artificial cream as defined in this Act unless—

- (a) the substance is cream as defined in this Act, or
- (b) where the substance is artificial cream as defined in this Act, the word "cream" is immediately preceded by the word "artificial."

(2) Every receptacle used for the conveyance of artificial cream for sale for human consumption, or containing artificial cream at any time when it is exposed for such sale, shall have the words "artificial cream" printed in large and legible type either on the receptacle itself or on a label securely attached thereto.

(3) If any person contravenes any of the provisions of this section, he shall be guilty of an offence against this Act.

2.—(1) Artificial cream shall not be manufactured, sold or exposed or kept for sale for human consumption except at premises registered with the Food and Drugs Authority:

* [19 & 20 Geo. 5.] [Ch. 32.] To be obtained from H.M. Stationery Office, price 2d. net.

Provided that this requirement shall not apply—

- (a) to the manufacture of artificial cream, by any person solely for his domestic purposes; or
- (b) to the manufacture on any premises of artificial cream for use in the preparation on those premises of some other article of food; or
- (c) to the sale, exposure or keeping for sale of artificial cream on any premises where it is not supplied otherwise than in the properly closed and unopened receptacles in which it was delivered to those premises.

(2) The Food and Drugs Authority shall keep a register of premises under this section, and shall on application being made by the owner or occupier of any premises enter the premises in the register and shall from time to time revise the register as occasion may require.

(3) Any officer of the Food and Drugs Authority duly authorised in that behalf by the authority may at all reasonable times enter and inspect any premises registered with the authority under this section.

(4) If a justice of the peace is satisfied by information on oath that there is reasonable ground for supposing that any unregistered premises are being used for the manufacture of artificial cream contrary to the provisions of this section, he may grant a search warrant authorising any such officer as aforesaid to enter and inspect the premises and to search for and seize any machine suitable for use in the manufacture of artificial cream.

(5) If any person uses any unregistered premises for the manufacture or sale of artificial cream in contravention of this section, or obstructs any such officer as aforesaid in the execution of his powers under this section, or fails to give any such officer all reasonable assistance in his power, or to furnish him with any information he may reasonably require, he shall be guilty of an offence against this Act.

3. Such of the provisions of the Public Health Acts, 1875 to 1926 (or, in London, the Public Health (London) Acts, 1891 to 1926), and the Milk and Dairies (Consolidation) Act, 1915, and of any order or regulation made under any of those Acts, as relate to cream (other than those relating to registration) shall apply to artificial cream.

4. It shall be the duty of every Food and Drugs Authority to enforce the provisions of this Act, and any expenses incurred by the authority for that purpose shall be defrayed as expenses under the Food and Drugs (Adulteration) Act, 1928:

Provided that this section shall not apply to such of the provisions of any Act, order or regulation applied by this Act as are enforceable by any other authority.

5.—(1) If any person commits an offence against this Act, he shall be liable on summary conviction to a fine not exceeding, in the case of a first offence, five pounds, in the case of a second or subsequent offence, fifty pounds, and in any case where the offence is a continuing offence, to a further fine not exceeding forty shillings for each day during which the offence continues.

(2) For the purposes of proceedings under this Act—

- (a) where artificial cream is sold or offered, exposed or kept for sale, it shall be presumed to be sold or offered, exposed or kept for sale for human consumption unless the contrary is proved;
- (b) where any article having the composition of cream or artificial cream is sold or exposed or kept for sale on premises registered under this Act, it shall be presumed to be artificial cream unless the contrary is proved.

(3) The provisions of subsection (6) of section twenty-seven and of sections twenty-nine and thirty of the Food and Drugs (Adulteration) Act, 1928, relating to offences and warranties under that Act, as set out with the appropriate modifications in the Schedule to this Act, are hereby incorporated with this Act and shall apply to proceedings under this Act.

6. In this Act—

“Food and Drugs Authority” has the same meaning as in the Food and Drugs (Adulteration) Act, 1928;

“Cream” means that portion of natural milk rich in milk fat which has been separated by skimming or otherwise;

“Artificial cream” means an article of food resembling cream and containing no ingredient which is not derived from milk except water or any ingredient or material which by virtue of the proviso to subsection (2) of section two of the Food and Drugs (Adulteration) Act, 1928, may lawfully be contained in an article sold as cream.

7. This Act shall apply to Scotland subject to the following modifications:—

(a) The following section shall be substituted for section three—

Such of the provisions of the Milk and Dairies (Scotland) Act, 1914, and of any order, regulation or byelaw made under that Act as relate to cream (other than those relating to registration) shall apply to artificial cream:

(b) The expression "defendant" shall mean "respondent," and the expression "information" shall mean "complaint."

8.—(1) This Act may be cited as the Artificial Cream Act, 1929.

(2) This Act shall come into operation on the first day of June, nineteen hundred and twenty-nine.

(3) This Act shall not extend to Northern Ireland.

SCHEDULE.

PROVISIONS OF FOOD AND DRUGS (ADULTERATION) ACT, 1928, APPLIED.

1. Where an employer is charged with an offence against this Act, he shall be entitled, upon information duly laid by him, to have any other person whom he charges as the actual offender brought before the court at the time appointed for hearing the charge, and if, after the commission of the offence has been proved, the employer proves to the satisfaction of the court that he had used due diligence to enforce the execution of this Act, and that the said other person had committed the offence in question without his knowledge, consent or connivance, the said other person shall be summarily convicted of the offence, and the employer shall be exempt from any penalty.

2. Subject to the provisions of this schedule a defendant shall be discharged from any prosecution under this Act for selling, or offering or exposing for sale artificial cream, if he proves to the satisfaction of the court that he had purchased the article in question as cream, and with a written warranty or invoice to that effect, and that he had no reason to believe at the time of the commission of the alleged offence that the article was not cream and that at that time the article was in the same state as when he purchased it.

3. A warranty or invoice shall only be a defence to proceedings under this Act if—

(a) the defendant has within seven days of the service of the summons sent to the prosecutor a copy of the warranty or invoice with a written notice stating that he intends to rely on it and specifying the name and address of the person from whom he received it and has also sent a like notice of his intention to that person; and

(b) in the case of a warranty or invoice given by a person resident outside the United Kingdom the defendant proves that he had taken reasonable steps to ascertain, and did in fact believe in the accuracy of the statement contained therein.

4. The person by whom the warranty or invoice is alleged to have been given shall be entitled to appear at the hearing and to give evidence, and the court may, if it thinks fit, adjourn the hearing to enable him to do so.

5. Where the defendant is a servant of the person who purchased the article under a warranty or invoice he shall be entitled to rely on the provisions of this schedule in the same way as his employer would have been entitled to do if he had been the defendant, provided that the servant further proves that he had no reason to believe that the article was not cream.

6. Every person who wilfully applies to an article in any proceedings under this Act a warranty or invoice given in relation to any other article, shall be guilty of an offence against this Act.

7. Every person who, in respect of artificial cream sold by him as principal or agent, gives to the purchaser a false warranty in writing, shall be guilty of an offence against this Act, unless he proves to the satisfaction of the court that when he gave the warranty he had reason to believe that the statements or descriptions contained therein were true.

8. Where the defendant in a prosecution under this Act has been discharged under the provisions of this schedule relating to warranties, any proceedings under this schedule for giving the warranty relied on by the defendant in the prosecution, may be taken as well before a court having jurisdiction in the place where the contravention of this Act took place as before a court having jurisdiction in the place where the warranty was given.

Ministry of Health.

THE Minister has sent the following Circular (No. 989) to the Clerks of Authorities administering the Food and Drugs Acts:—

ARTIFICIAL CREAM ACT, 1929.

SIR,

1. I am directed by the Minister of Health to draw the attention of the Food and Drugs Authority to the Artificial Cream Act, 1929, which will come into operation on the 1st June next. The substance whose sale and manufacture the Act is designed to regulate is a cream substitute which has hitherto been commonly known as reconstituted cream and is usually prepared by emulsifying butter, dried skimmed milk and water. The definition in Section 6 of the Act is however drawn in sufficiently wide terms to include any article of food resembling cream and containing nothing but the ingredients of cream.

2. Sub-section (1) of Section 1 provides that where any substance purporting to be cream or artificial cream is artificial cream, it shall not be sold under a description or designation including the word "cream" unless that word is immediately preceded by the word "artificial." This provision is more specific than that of Section 2 of the Food and Drugs (Adulteration) Act, 1928, and, as the Authority are no doubt aware, the machinery of that Act has generally been considered to be inadequate to prevent the sale of artificial cream as cream, since if due precautions are taken in blending the ingredients of artificial cream an analyst cannot distinguish it from cream.

3. The new Act contains a number of further provisions for facilitating the enforcement of the principal requirement. Under Sub-section (1) of Section 1 receptacles used for conveying artificial cream or for containing it when it is exposed for sale must be labelled with the words "artificial cream" in large and legible type; Section 2 requires that with certain specified exceptions premises where artificial cream is manufactured or sold must be registered with the Authority; and Section 5 (2) (b) provides that where an article having the composition of cream or artificial cream is sold on premises so registered it shall be presumed to be artificial cream unless the contrary is proved.

4. This circular will be placed on sale, and further copies may be obtained directly from His Majesty's Stationery Office or through any bookseller. Copies are being sent to the Medical Officer of Health and the Public Analyst.

I am, sir, your obedient servant,

May 24th, 1927.

R. B. CROSS (*Assistant Secretary*).

Ministry of Agriculture and Fisheries.

FERTILISERS AND FEEDING STUFFS ACT, 1926.

PROCEDURE UNDER SECTION 13(3).

THE following letter (C.C. 5286) has been sent by the Ministry to the Clerks of Local Authorities administering this Act:—

SIR,

I am directed to inform you that several cases have already arisen in which persons objecting to the certificate of an agricultural analyst in respect of a sample taken under the provisions of the above-mentioned Act, have requested that a part of the sample should be submitted to the Government Chemist for analysis. It seems to be desirable, therefore, in order to obviate delay in similar cases which may arise in the future, that the most convenient procedure for adoption in these cases should be laid before the responsible officers of Local Authorities.

(2) It will be observed that Section 13(3) of the Act provides that:—

"If the person by or on whose behalf the sample of an article is taken and analysed, or the owner or seller of the article, objects to the certificate of the agricultural analyst, the person objecting thereto shall, on payment of such fee as may be fixed by the Treasury, be entitled to have submitted to the Government Chemist the part of the sample retained by the agricultural analyst and to have that part analysed by him and to receive from him a certificate of the result of his analysis."

(3) In any case where objection is taken to the certificate of the agricultural analyst, arrangements should be made to send to the Government Chemist, as soon as possible, AND BY REGISTERED POST:—

- (i) The part of the sample retained by the agricultural analyst in accordance with Section 13(2).
 - (ii) Copy of the statutory statement or warranty or of the particulars marked on or indicated by a mark applied to the article (see Section 13(4)).
 - (iii) Copy of the agricultural analyst's certificate, which may be of assistance to the Government Chemist in concentrating attention upon the specific point in dispute.
 - (iv) The name and address of the person requiring the analysis to be made, and from whom the fee is recoverable.
- (4) The address of the Government Chemist is

GOVERNMENT LABORATORY,
CLEMENT'S INN PASSAGE,
STRAND, LONDON, W.C.2.

(5) The fee fixed by the Treasury for the analysis of a sample by the Government Chemist is £2 2s. 0d., but it is not necessary for the Local Authority to take any steps to collect this sum.

I am, &c.,

Feb. 27th, 1929.

(Signed) A. P. A. DOBSON.

United States Department of Agriculture.

CERTIFICATION OF COAL-TAR FOOD COLOURS.*

THE PERMITTED DYES.

Two new colours, Ponceau SX and Sunset Yellow FCF, are hereby added to the list of coal-tar dyes accepted for certification by the department. The following coal-tar dyes are now accepted for certification as described on pages 4 to 6 of Service and Regulatory Announcements, Food and Drug No. 3:

Red shades.—80. Ponceau 3R. 184. Amaranth. 773. Erythrosine, Ponceau SX.

Orange shade.—150. Orange I.

Yellow shades.—10. Naphthol Yellow S.; 640. Tartrazine; 22. Yellow AB.; 61. Yellow OB.; Sunset Yellow FCF.

Green shades.—666. Guinea Green B.; 670. Light Green SF Yellowish; Fast Green FCF.

Blue shade.—1180. Indigotine.

The numbers preceding the names refer to the colours, as listed in the Colour Index published in 1924 by the Society of Dyers and Colourists of England, which gives the composition of these dyes. Names not preceded by numbers are not listed in the Colour Index. The composition of such dyes will be furnished on application to the Food, Drug, and Insecticide Administration.

R. W. DUNLAP,

Acting Secretary of Agriculture.

WASHINGTON, D.C., April 2, 1929.

* Service and Regulatory Announcements, Food and Drug No. 3, Supplement No. 1.

A Correction.—We regret that in the May issue (p. 290) the word "tabloids," which should only be applied to the products of Messrs. Burroughs, Wellcome & Co., was inadvertently used for "tablets."—EDITOR.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Distinction between Pressed and Extracted Cacao Butter. Aufrecht. (*Chem. Ztg.*, 1929, 53, 318.)—The means by which cacao butter has been separated may be ascertained as follows: 2 grms. of the butter are dissolved in 5 c.c. of chloroform in a dry test-tube, the clear solution obtained being gently mixed with 5 c.c. of fuming hydrochloric acid (1.192; about 37 per cent.). In presence of extracted cacao shell butter, the lower liquid layer turns first pale green, and, after a minute, dark green. When heated at 50° C. for 2 minutes with 2 drops of concentrated nitric acid (1.42), this mixture becomes reddish-brown with a violet tinge, or, in the case of cacao butter extracted from residues, brownish-yellow. After standing for five minutes at 50° C., the colour changes to brownish-violet. With the expressed butter, the mixture remains colourless, both when cold and when heated. This reaction detects an addition of 20–25 per cent. of cacao butter extracted from either shells or residues. No trace of a colour reaction is obtained with ordinary or hardened coconut fat, palm kernel fat, hardened whale oil, vegetable hard butter ("Cocola" and "Kernal"), French vegetable fat ("Banka"), or English hard butter ("Makon").

An even sharper distinction is possible with sulphuric acid. If a solution of 2 grms. of the extracted or residue butter in 5 c.c. of chloroform is treated with 5 drops of sulphuric acid (1.84), the mixture becomes at once deep violet, this changing to brownish-violet after 2 minutes in a water-bath at 50° C. With mixtures of the expressed and extracted butters the colour is pale brown (cold) or deep brownish-violet (50° C.). Pure expressed cacao butter gives a colourless (cold) or a reddish-yellow liquid with a violet tinge (50° C.). Stearin, coconut fat, palm kernel fat, refined Dutch vegetable fat, vegetable hard butter, and hardened fats show no colour reaction. In mixtures of extracted and pressed cacao butter about 10 per cent. of the former is detectable in this way. With mixtures of doubly refined extracted cacao butter with the expressed butter the hydrochloric acid test fails, but the sulphuric acid test detects 20–25 per cent. of the former. When chocolates, etc., are to be examined, the fat is extracted with ether, the filtered ethereal solution evaporated at a low temperature, and the fat dissolved in chloroform and tested as above.

T. H. P.

Fachini's Reaction for the Detection of Olive Residue Oils. R. Marcille. (*Ann. Falsif.*, 1929, 22, 163–166.)—Since Fachini's reaction (*ANALYST*, 1926, 51, 416, 636) may give positive results with true olive oils, it cannot be regarded as specific for residue oils. The depth of colouring depends on the quality of the oil, and particularly on the amount of resinous material which may have permeated into the oil, owing to decomposition of the olives before treatment. The reaction is useful for characterising olive oil in mixtures on the assumption that all olive

oils give some colour, but that kernel oils do not, and for deciding if oils of low acidity contain refined oils of inferior quality, without specifying if these are olive residue oils.

D. G. H.

Luminescence of a Genuine Dutch Lard in Ultra-Violet Light. A. van Druten. (*Z. Unters. Lebensm.*, 1929, 57, 60-62.)—Contrary to experience (*cf.* van Raalte, *ANALYST*, 1929, 54, 110, and Weiss, *id.*, 178) genuine Dutch lard from pigs slaughtered in the autumn of 1928 gave a bright blue to blue-violet fluorescence in ultra-violet light at 60° C. The intensity was increased after bleaching with 4 per cent. of fuller's earth and 0.25 per cent. of norit, but was decreased after heating at 140° C. In the case of the solid lard the fluorescence appeared on the surface.

J. G.

American Safflower Oil. G. S. Jamieson and S. I. Gertler. (*Oil and Fat Ind.*, 1929, 6, 11-12.)—The characteristics of hot-pressed oil from safflower seed grown in Montana were: Sp. gr., 25°/25° C., 0.9243; n_D^{25} , 1.4744; saponification value, 190.5; unsaponifiable matter, 0.59 per cent.; iodine value (Wijs), 149.1; Reichert-Meissl value, 0.2; Polenske value, 0.1; acetyl value, 12.5; acid value, 5.5; saturated acids (corrected), 5.9; and unsaturated acids (corrected), 87.7 per cent. (iodine value, 156.0). The unsaturated acids consisted of linolenic, 0.16; linolic, 71.82; and oleic 28.02 per cent., and the saturated acids of myristic, 0.7; palmitic, 66.2; stearic, 25.2; arachidic, 6.8; and lignoceric, 1.05 per cent. The oil has a greater drying power than sunflower or soya bean oils, and the press-cake is useful as a cattle food.

D. G. H.

Fruits and Seeds of *Hydnocarpus Woodii* from North Borneo. (*Bull. Imp. Inst.*, 1929, 27, 12-16.)—The air-dried kernels of these seeds, from fruits received in 1925, contained 7.8 per cent. of moisture, and yielded 57.4 per cent. of oil as a hard, cream-coloured solid having sp. gr. 0.8989 at 100°/15° C., acid value 32.8, saponification value 202.4, iodine value (Hübl, 17 hours) 85.8, unsaponifiable matter 0.5 per cent., n_D^{20} , 1.471; m.pt. 28.5° C., α_D^{20} (in chloroform) +53.1°; the fatty acids had solidification pt, 44.6° C., α_D^{20} (in chloroform) +54.4°. A second sample of kernels, obtained in 1927, contained 8.1 per cent. of moisture, and yielded 55.4 per cent. of oil with α_D^{20} +48.9°, and α_D^{20} of the fatty acids +49.8°, both in chloroform. From the oil, chaulmoogric and hydnocarpic acids were isolated by fractional distillation of the mixed ethyl esters under reduced pressure, followed by repeated crystallisations of the acids. Chaulmoogric acid gave m.pt. 67-68° C., $[\alpha]_D^{20}$ +61.9°, iodine value 89.3, percentage of silver in the silver salt 27.2; the corresponding figures for hydnocarpic acid were 58-59° C., +68.2°, 99.5, and 29.8, respectively. Thus the oil of *Hydnocarpus Woodii* seeds contains the glycerides of these two acids, and hence resembles that of *Hydnocarpus Wightiana*, which is largely used for treating cases of leprosy.

T. H. P.

Sampling Apples in the Orchard for the Determination of Arsenical Spray Residue. J. W. Barnes. (*Ind. Eng. Chem.*, 1929, 21, 172-174.)—Separate analyses of 300 apples from 4 trees, showed that the arsenical residue

varied from 0.000 to 0.031 grain of arsenic per apple, the average being 0.011. The range for weight was from 0.004 grain to 0.095 grain per pound of fruit, with an average of 0.031 grain, and the range for area was from 0.05 grain to 1.30 grain per 1000 square inches of area of fruit, the average being 0.45 grain. The trees had received four applications of lead arsenate in a spray of 2 pounds to 50 gallons of water, the last treatment being on July 1st, and the apples were gathered in the middle of October. The following formula is given for calculating the area of an apple from its weight:— $A = 0.842 (W)^{2/3}$, where A is the area in sq. inches and W the weight in grms. The results obtained indicate that it is necessary to analyse a sample of about 50 apples picked at random in order to obtain a value with a probable error of 5 per cent. for the mean arsenical residue per pound of fruit.

W. P. S.

Preparation of Banana Vinegar. H. von Loesecke. (*Ind. Eng. Chem.*, 1929, 21, 175–176.)—A banana mash, consisting of the pulp and peel of ripe fruit, was pasteurised at 76° C. for forty-five minutes (without addition of water), cooled, and fermented with *Saccharomyces ellipsoideus*. Fermentation was complete in fourteen days at 20° to 23° C., and the yield of banana cider, containing 9 per cent. of alcohol (by vol.), amounted to 56 per cent. of the weight of fruit taken. The cider was mixed with one-third its volume of strong vinegar and allowed to trickle through a column of beechwood shavings previously boiled in water, dried, and impregnated with vinegar. About fifty hours were required to convert 1 litre of cider into vinegar. Better results were obtained by the Orleans process, in which the cider was mixed with one-fourth its volume of vinegar, put into flasks, and the latter closed with plugs of cottonwool. Acetification was usually complete after seventy-five days at 30° C. The vinegar was finally filtered, clarified with kieselguhr, and pasteurised for one minute at 60° C. The banana vinegar thus prepared had a good colour and pleasing aroma and taste; it contained from 4 to 7 per cent. of acetic acid.

W. P. S.

Manganese in Foodstuffs. C. Newcomb and G. Sankaran. (*Indian J. Med. Res.*, 1929, 16.)—The proportions of manganese in a large number of substances were determined. They differed widely both in different substances and in samples of the same food. The mean amounts found for some of these include, in mgrms., per kilo. (pts. per million): Arrowroot, 1; barley, 10; oatmeal kernel, 348; rice, polished 9.5, unpolished 17, husk 130; potato starch, 2; rice starch, 11; cod liver oil, 0; sesame oil, 4; olive oil, 0; betel nut, 39; chillies, 14; pepper, 64; cabbage, 1.3; coconut fresh "meat," 15; onion, 33; tomato, 31; cane sugar, 0; egg yolk, 2.5; egg shell, 17; linseed meal, 168; milk, 1; teas, 115–546; and tea infusion, 0.6. In the case of the cereals the manganese is largely lost in the preparation for market. Five grms. or more of food stuff are ashed, any chlorides removed if present to appreciable extent, and if the ash is voluminous and insoluble in dilute nitric acid, it is fused in a nickel vessel with potassium and sodium carbonates and a little potassium nitrate. The fused mass is extracted with water, the extract poured directly into twice the quantity of

dilute nitric acid required for neutralisation, and 6 c.c. of 85 per cent. phosphoric acid, 25 c.c. of silver nitrate (1.5 grm. per litre) and water to make up to about 200 c.c. added, and the whole boiled. Solid ammonium persulphate is then added, little by little, and after a short time the solution will turn pink and the turbidity clear up. The liquid is heated to boiling, another pinch of ammonium persulphate is added, the solution made up to 250 c.c., and the amount of manganese determined by reading against a standard permanganate solution. If there is but little ash, or if it is completely soluble in dilute (1:5) nitric acid, the ash is extracted with dilute nitric acid, any insoluble matter filtered off through a small paper, the paper moistened with a solution of sodium and potassium carbonates, and a little potassium nitrate, dried, burnt on a platinum wire and the bead dissolved in the nitric acid extract. An addition of 2.4 c.c. of phosphoric acid and 10 c.c. of silver nitrate per 100 c.c. of final bulk of solution is made, and the pink colour developed as before. When the amount of permanganate was not less than 0.1 mgrm. per 100 c.c. a Kober's colorimeter was used for the comparison, and with weaker solutions Nessler glasses.

D. G. H.

Zinc Contents of the Principal Vegetable Foodstuffs. G. Bertrand and B. Benzon. (*Bull. Soc. Chim.*, 1929, 45, 168-175.)—To determine zinc in vegetable materials, from 200 grms. for seeds and tegumentary tissues to 1000 or 1500 grms. for leafy parts or parenchymatous organs are heated on a water-bath or in an oven to remove the water, and then carefully ignited in a muffle furnace to destroy the organic matter. The zinc in the residue is then determined by the calcium zincate method. The results obtained for a large number of different materials show that the pulp of fruits and etiolated leaves contain less than 1 mgrm. of zinc per kilo., whilst parenchymatous roots (carrots, etc.), orange pulp, lemon juice, leaves poor in chlorophyll, figs, chestnuts, and grapes contain 1-2 mgrms. Higher proportions appear in organs rich in chlorophyll: thus carrot leaves and lucerne contained 4 mgrms., radish 4.5, cabbage lettuce 4.7, cress 5.6, spinach 6.2, dandelion 9.7. Mature potatoes contained 5, *Boletus edulis* 5.1, bakers' yeast 12.4, garlic 10, onion 13.8, cereals 12 to 19.5, soya beans 20, vetch seeds 23, lentils 24.4, peas 44.5, haricots 52.5, cocoa beans, buckwheat and sweet almonds 10, arachis nuts 16, sunflower seeds 17, dried walnuts 20, pine kernels 55.5, hemp seed 82.6, polished rice 2.5, rice bran 30, white flour (75 per cent. extraction) 6 to 7, wholemeal flour 10 to 15. T. H. P.

Application of the Method of Hagedorn and Jensen to the Determination of Larger Quantities of Reducing Sugars. C. S. Hanes. (*Biochem. J.*, 1929, 23, 99-106.)—A modification of the method of Hagedorn and Jensen (*Biochem. Z.*, 1923, 135, 46) is described which enables about 10 times as much reducing sugar as before to be determined. The original method was for the measurement of the reducing sugar in the filtrates from 0.1 c.c. samples of blood, with an upper limit of 0.385 mgrm. of glucose. It consisted in the reduction of potassium ferricyanide, when heated in alkaline solution with certain reducing substances, to ferrocyanide, precipitation of the ferrocyanide as the double potassium zinc salt, and determination of the residual ferricyanide by treatment with excess of

potassium iodide and acidifying. The iodide reduces the ferricyanide quantitatively, and equivalent iodine is liberated according to the equation : $2\text{H}_3\text{Fe}(\text{CN})_6 + 2\text{HI} = 2\text{H}_4\text{Fe}(\text{CN})_6 + \text{I}_2$, and titrated with thiosulphate. Except as regards the volumes and concentrations of the various reagents used, no essential change has been made. The following solutions are needed for the new method :—*Solution A*.—Potassium ferricyanide (8.25 grms.) and anhydrous sodium carbonate (10.6 grms.) are made up to 1 litre with distilled water; this solution must be kept for 2 to 3 days before use, stored in a bottle with an opaque jacket. *Solution B*.—Potassium iodide (12.5 grms.), zinc sulphate (25.0 grms.) and sodium chloride (125.0 grms.) are made up to 500 c.c. with distilled water. Before use this solution must be filtered through 2 thicknesses of filter paper to remove traces of iodine which appear on storing. *Solution C*.—Glacial acetic acid (5 c.c.) diluted to 100 c.c. with distilled water. *Solution D*.—Merck's soluble starch (1 gm.) in about 20 c.c. of cold water is washed into 60 c.c. of boiling water, boiled for 2 minutes, 20 grms. sodium chloride added, the liquid cooled, and made up to 100 c.c. This solution keeps for several months. *Solution E*.—An approximately *N*/75 sodium thiosulphate solution, used in a 10 c.c. burette, graduated in 0.02 c.c. divisions. About 10 litres are made up with boiled-out water (3.33 grms. sodium thiosulphate per litre). This is protected from carbon dioxide by a soda-lime tube, and run through a siphon to the burette. It is standardised against a potassium iodate solution (0.80 grms. in a litre). Five c.c. of iodate solution are pipetted into a boiling tube to which are added 5 c.c. of 2 per cent. potassium iodide solution, and 3 c.c. of solution C. The liberated iodine is titrated with the thiosulphate solution, one drop of solution D added as indicator when the colour is pale yellow, and titration continued to the disappearance of the blue colour. The value for the normality is found from the expression

$$\frac{\text{Grm. KIO}_3 \text{ per litre} \times \text{vol. of pipette (c.c.)}}{35.67 \times \text{vol. of thiosulphate required (c.c.)}}$$

and the volume of thiosulphate required is about 9 c.c. The sugar determinations are carried out in boiling-tubes (1 × 7 ins.), with glass bulbs with an inch of tubing left attached as covers. Five c.c. of solution A are pipetted into a boiling-tube, the pipette being allowed to drain a standard time, and then 5 c.c. of the solution whose reducing power is to be determined (or less than 5 c.c. + water to make up to 5 c.c.). A water blank is then prepared—5 c.c. of solution A and 5 c.c. of distilled water. All drops on the sides must be mixed in, and the tubes are then covered with glass bulbs, placed in a boiling water bath, 2 or 3 in. deep, for 15 minutes, and cooled for 3 minutes in cold running water. On adding from a rapid pipette 5 c.c. of solution B a white flocculent precipitate appears and iodine is set free; 3 c.c. of solution C are added, and the liberated iodine is titrated against the standardised thiosulphate solution in the same boiling tube. The difference between the water blank value (WB), and the reading obtained with the experimental solution (R) gives the thiosulphate equivalent of the ferricyanide reduced by the experimental solution. Standardisation data are given for glucose and maltose, and

shown in a graph. Water blank values need only be determined once or twice a day, and 18 determinations can be done in an hour in batches of 5 or 6. An important advantage over copper methods is pointed out in the fact that variations in the amounts of dissolved oxygen in sugar solutions do not affect the reducing values arrived at by the ferricyanide method.

P. H. P.

Beta-anthraquinone-monosulphonic Acid as a Microchemical Reagent for Alkaloids, etc. L. Rosenthaler. (*Amer. J. Pharm.*, 1929, 101, 196-197.)—Beta-anthraquinone-monosulphonic acid (Beta-A acid) is a general alkaloidal precipitant, although some of the precipitates are not quite insoluble, and in many cases are amorphous. Crystals result from the addition of the following crystalline alkaloidal bases or salts to a 10 per cent. solution of the Beta-A acid: Aniline (sulphate), pink drops then bundles of needles and spears; antipyrine: drops, then sheaves of small needles; atropine sulphate: amorphous, then "bunches" of needles; hydrastinine (hydrochloride): drops, then a micro-crystalline precipitate, at last small rectangular, strongly polarising leaves; nicotine: amorphous, then small aggregates like calcium oxalate; novocaine (hydrochloride): deep orange-red drops, later bunches of needles; tropacaine (hydrochloride)—drops, then bunches of needles. If a small crystal of cinchonine sulphate is placed in a drop of Beta-A acid, bubbles appear on the crystal, but may disappear, and small granules becoming larger or even spherocrystalline masses of needles follow. With salts of quinine and cinchonidine, bubbles only are formed; the forms with quinine sulphate have regular notchings or may be granular; with emetine hydrochloride they are mostly free from notchings. These formations are only produced with the salts, and not usually with the free bases, in consequence of lower solubility. The reaction is considered a "topochemical" one, the typical development of which depends on the drug being from some particular locality.

D. G. H.

Insecticidal Value and Determination of Pyrethrin I and II in *Pyrethrum cinerariaefolium*. I. F. Tattersfield and R. P. Hobson. (*J. Agric. Sci.*, 1929, 19, 266-296.)—Pyrethrin I and II have been isolated from *Pyrethrum cinerariaefolium*, and, while both are highly toxic (to *Aphis rumicis*), pyrethrin I is about 10 times more so than pyrethrin II. Samples of flowers grown from the same seed on the same soil vary in pyrethrin content within fairly wide limits according to the season. The total amount of the two toxic principles in flowers from 10 localities grown from the seed of the same origin varied in one season from 0.71 to 1.17 per cent. The micro-methods used for determination are adaptations of Staudinger and Harder's macro-methods (*Amer. Acad. Scient. Fennicae A*, 1927, 18), and the results agreed with observed insecticidal properties. In the acid method 10 grms. of ground flowerheads (50 grms. of stalk) are extracted with petroleum spirit, the solvent evaporated in carbon dioxide, the residue extracted with 4 (stalk 6) lots of 2.5 c.c. of absolute methyl alcohol, and the extracts filtered through cotton wool into a long-necked 100 c.c. flask. The solution is treated with 4 c.c. of *N* sodium hydroxide in methyl alcohol, boiled under a condenser for

6-8 hours, the alcohol removed by warming, the soaps dissolved in-water, and 6 c.c. of *N* sulphuric acid added. The acid liquid is distilled, and after 50 c.c. of distillate have been taken for determination of volatile acid another 100 c.c. are collected. The first 50 c.c. are extracted with 50 c.c. of petroleum spirit, the extracts washed, and after evaporation of the ether the aqueous liquid is titrated with 0.2 *N* sodium hydroxide solution. To the hot residue in the flask (not over 40 c.c.) 0.2 grm. of calcium sulphate is added, and after standing overnight the liquid is filtered into the automatic extractor (illustrated in the text) and extracted with methylated ether for 8 hours, after which 20 c.c. of water are added to the extract and the ether taken off. The aqueous layer is filtered and the dicarboxylic acid titrated with 0.2 *N* sodium hydroxide, of which 1 c.c. is equivalent to 3.36 mgrms. of monocarboxylic acid, 6.6 mgrms. of pyrethrin I, 1.90 mgrms. of dicarboxylic acid or 3.74 mgrms. of pyrethrin II. The semicarbazone method, described in detail, determines the sum of the 2 pyrethrins, and is used as a confirmation of the acid method. The analytical results obtained for a series of pyrethrum samples agreed with their observed insecticidal action on *Aphis rumicis*. Data are not yet sufficient to show significant correlation between size of flower heads and content of poison, or to draw conclusions as to effect of external conditions.

D. G. H.

Preservation of Anaesthetic Ether. C. L. Hewer. (*Lancet*, 1929, 770-771.)—The oxidation to which ether is prone may be prevented by treating the ether with carbon dioxide and then storing it in copper containers. When anaesthetic gases are bubbled through ether for long periods, the rate of decomposition of the ether will be greatly diminished if there is an adequate area of copper both above and below the surface level of the liquid.

T. H. P.

Colorimetric Determination of Ergot in Flour. F. S. Okoloff. (*Z. Unters. Lebensm.*, 1929, 57, 63-71.)—For rye flour 10 grms. dried for 1 hour at 110° C., are shaken with a mixture of 500 c.c. of chloroform and 60 c.c. of alcohol (sp. gr. 1.415 to 1.420), and the floating portion filtered off after 1 hour, dried and shaken with 30 c.c. of ether and 1 c.c. of sulphuric acid (1 in 4). The next day the glutinous precipitate is filtered off, the flask and paper washed with ether till 40 c.c. of filtrate are obtained, and 2 c.c. of a saturated solution of sodium bicarbonate added. After the mixture has been shaken, the coloured aqueous layer is transferred to the tube of a Walpole colorimeter, and the colour matched by means of a suitable combination of two standards:—(1) A solution of 0.1 grm. of carmine in a mixture of 5 c.c. of concentrated ammonia and 95 c.c. of water. Portions of from 0.05 to 0.5 c.c. are diluted to 10 c.c., preserved with 2 drops of formalin, and stored in the dark in stoppered tubes. (2) A solution of 0.05 c.c. of methyl orange in 100 c.c. of water, of which 0.2 to 0.5 c.c. portions are diluted to 50 c.c. after the addition of 2 c.c. of 0.1 *N* sodium hydroxide solution. The percentage of ergot is given by the number of c.c. in the carmine solution which exactly matches, the methyl orange solution being used only for the compensation of the yellow colour. If the colour is too intense 0.1 *N* sodium hydroxide solution

is added to the solution, and since 2 c.c. reduces the colour by one-half, the true percentage of ergot is obtained by multiplying the carmine value by half the number of c.c. added. With wheat flour 20 grms. of sample are shaken with 50 c.c. of ether and 5 c.c. of sulphuric acid (1 in 4), filtered after a day, the filtrate diluted to 60 c.c., and the above procedure followed. In this case, however, 0.3, 0.4 and 0.5 per cent. of ergot correspond with 0.45, 0.55 and 0.65 c.c. of carmine solutions, respectively, the smaller quantities being exactly equivalent as before. If the colour is reduced by alkali the ergot percentage must be multiplied by half the number of c.c. used. The methods were shown to be independent of the type or age of the sample, the maximum recorded error for quantities up to 3 per cent. of ergot being 0.2 per cent.

J. G.

Biochemical.

Determination of Ergot in Flour by a Serological Method. F. S. Okoloff and I. G. Akimoff. (*Z. Unters. Lebensm.*, 1929, 57, 72-76.)—An antigen was prepared by the intravenous injection of rabbits with 1.0 to 5.0 c.c. of an extract of ergot from which water-soluble poisons (*e.g.* alkaloids, amines, etc.) were removed by the following treatment:—The de-fatted, dried and powdered ergot was extracted twice with water for 24 hours, the residue dried, and well mixed with physiological salt solution containing 0.5 per cent. of sodium hydroxide solution and chloroform. After 24 hours the mixture was neutralised with a 10 per cent. solution of phosphoric acid and filtered. If the immunisation was extended over a period of 2 months (Raiski) a titre value, for the serum, of 1:20,000 was obtained. The precipitin ring test was then carried out in an agglutination-tube with 2 c.c. of serum and 0.5 c.c. of a filtered solution prepared by extracting 20 grms. of sample with 100 c.c. of physiological salt solution for 24 hours. An ergot content of 0.1 to 0.5 per cent. gave sharply defined rings after incubation for 25 minutes at 37° C., 0.05 per cent. showed more diffuse rings, which were intensified after 35 minutes at room temperature, whilst 0.02 per cent. gave a doubtful ring or an opalescence, and ergot-free flour gave no reaction. Tests for specificity on 11 weeds gave indefinite results, which, however, are not considered to detract from the value of the method.

J. G.

Factors affecting the Yield and Quality of Milk. 1. The Age of the Cow. R. R. Kay and H. C. McCandlish. (*J. Agric. Sci.*, 1929, 19, 342-372.)—As a result of investigating the records of 738 Ayrshire cows for 4380 lactations, it is shown that up to 7 years of age (maturity) milk and butterfat production increase, but there is a tendency to a slightly lower fat percentage with advance of age, probably owing to the fact that, as the milk yield changes, the fat yield does so in the same direction, but at a slower rate. The 3-year-old fat percentage is significantly higher than for other ages, averaging 3.87, falling to 3.76 in the 4-year-old group, and remaining at 3.74-3.77 to 5 to 8 years, and then gradually falling. At 12 and 13 years it averaged 3.23 and 3.45 per cent. The increase of production

with age is partly due to growth of the secretory tissue of the udder and to general body growth, and with maturity is probably more closely associated with high initial production than with persistency of production. Correction factors for age are suggested as follows:—Age 3 years: milk yield 1.16, fat yield 1.13; 4 years, 1.12, 1.12; 5 years, 1.06, 1.05; 6 years, 1.03, 1.03; 7 years, 1.00, 1.00.

D. G. H.

Determination of Tryptophan by means of *p*-Dimethylaminobenzaldehyde. W. J. Boyd. (*Biochem. J.*, 1929, 23, 78–82.)—It has been found that errors can arise in the determination of tryptophan in proteins by the method of May and Rose (*J. Biol. Chem.*, 1922, 54, 213), (1) through unequal illumination of the reacting mixtures, and (2) through the presence of reducing substances such as hydrogen sulphide or aldehydes. For the May and Rose method, 0.1 grm. protein is added to a mixture of 50 c.c. concentrated hydrochloric acid, 50 c.c. water and 1 c.c. of a 5 per cent. solution of *p*-dimethylaminobenzaldehyde in 10 per cent. sulphuric acid. The mixture is incubated for 24 hours at 36° C., and then left for 24 hours or longer at room temperature. When tryptophan is present the solution forms a blue colour, which is compared in a colorimeter with the colour given by caseinogen under the same conditions, and tryptophan is calculated on the assumption that caseinogen contains 1.5 per cent. of tryptophan. As a result of a study of the following factors, (1) effect of reducing substances, (2) effect of oxidising agents, and (3) effect of light, it is shown that the development of the colour is an oxidation process which proceeds slowly in dull light and more rapidly in bright light, and is not nearly complete in a period of 4 weeks in ordinary diffused daylight in the laboratory. The addition of a trace of an oxygen carrier or oxidising agent after hydrolysis of the protein hastens the process. If the oxygen carrier were added at the same time as the reagent, it would alter the aldehyde rapidly before it had time to combine with the tryptophan. Therefore, the best way to avoid the disturbing effects of varying illumination, and of reducing substances, is by the addition of a little sodium nitrite, nitric acid or hydrogen peroxide. In making the test, 3 drops of 0.5 per cent. sodium nitrite solution should be added to the reaction mixture after 24 hours' incubation at 36° C. and 3 days at room temperature, and again after a further 3 days, and the colorimetric comparison should be made next day or later. By this modified method higher values for the tryptophan content of cod-muscle protein and edestin are obtained than by the unmodified method of May and Rose. According to Jones, Gersdorff and Moeller (*J. Biol. Chem.*, 1924, 62, 183) the tryptophan content of caseinogen is assumed to be 2.2 per cent.

P. H. P.

Characterisation of the Anthocyanins and Anthocyanidins by means of their Colour Reactions in Alkaline Solutions. A. Robertson and R. Robinson. (*Biochem. J.*, 1929, 23, 35–40.)—It has recently been shown by Fear and Nierenstein (*Biochem. J.*, 1928, 22, 615) that the colour reactions of the anthocyanins, which are indicators, should be examined in solutions of definite pH . Accordingly the authors have examined the reactions of the anthocyanidins in a

range of buffered solutions, and have found that this method is by far the most reliable for purposes of comparison and characterisation; it is of even greater value in this connection than a study of the absorption spectrum, for by its means various properties, such as *pseudo*-base formation and colour base precipitation, ease of oxidation, etc., are incidentally revealed, whereas different anthocyanidins, such as peonidin and malvidin, may exhibit identical absorption spectra. The buffer solutions used consisted of phenylacetic acid, boric acid and potassium dihydrogen phosphate (0.02 grm. mol. each), together with *n* c.c. of 0.2 *N* sodium hydroxide, dissolved in water and made up to 1000 c.c. The approximate P_H of each solution, found by indicators, is given, and the results obtained with apigeninidin chloride, pelargonidin chloride, cyanidin chlorides, 5-*o*-benzoylcyanidin chloride, peonidin chloride, malvidin chloride, cyanin chloride and malvin chloride. Results with other anthocyanins will be recorded later. It is hoped that the data will be found useful for the identification of anthocyanidins derived from natural sources. Chrysanthemin chloride has been proved to be the 3-glucoside of cyanidin chloride. Contrary to the results of Nierenstein, the authors emphatically affirm that pure synthetic 3:5:7:3':4'-pentahydroxyflavylium chloride, best prepared by hydrolysis of its benzoyl derivative, exhibits no divergencies from cyanidin chloride, and that the constitution of cyanidin chloride in its main structural outlines is firmly established.

P. H. P.

Occurrence of Sucrase in Must and Wine. C. von der Heide and H. Mändlen. (*Z. Unters. Lebensm.*, 1929, 57, 13-36.)—The presence of sucrase in wine may be demonstrated by the gradual decrease in specific rotation of sucrose. Sucrase was detected in wines, grapes and musts. Its effect is particularly marked with new wines and wines containing yeast deposits, but in the course of time it becomes gradually inactive, probably on account of the combined influence of acid and alcohol. The actual life of the sucrase depends on the sugar, alcohol and acid concentrations, and on the temperature of storage, but is not usually more than 5 years. The enzyme is derived from the yeast or the grapes, and is partly or completely destroyed by heat. The conclusions of previous workers are critically discussed in the light of these results.

J. G.

Specific Colour Reaction for Ergosterol. O. Rosenheim. (*Biochem. J.*, 1929, 23, 47-53.)—The unique function of ergosterol as the parent substance of vitamin *D* made it desirable to find a colour reaction for it, by means of which it could be detected in the presence of other sterols. The property of formaldehyde of moving the colour from the red into the blue part of the spectrum in the usual colour reactions of sterol suggested a method. It was found that ergosterol gives a characteristic blue colour reaction with chloral hydrate, and also with trichloroacetic acid, whilst all the other naturally occurring sterols investigated, when purified from ergosterol, remain colourless under the same conditions. A few crystals of ergosterol, added to about 0.5 grm. of chloral hydrate, liquefied by warming on a water-bath, dissolve, and immediately give rise to a carmine red solution (absorption band $500\mu\mu$), which changes within a minute into a green,

and finally into a deep blue, which persists for a considerable time. Esters of ergosterol react in the same way. The colour is discharged rapidly by water or alcohol, but a saturated aqueous solution of chloral hydrate (80 per cent.) reacts typically when a drop of concentrated hydrochloric acid is added. Ergosterol dissolved in freshly distilled anhydrous chloral gives the same colours on the addition of one drop of water. An aqueous solution of trichloroacetic acid (9:1), added to ergosterol dissolved in a few drops of chloroform gives an immediate red solution (band at $500\mu\mu$), which gradually changes into a clear blue (bands at $570\text{--}580$ and $650\text{--}680\mu\mu$), without showing the intermediate green phase. This occurs at room temperature, and the final blue solution may be diluted with the reagent or with chloroform. The sensitiveness of the reaction is of about the same order as that of the usual sterol reactions, *i.e.* 0.005 mgrm. may be determined. In contradistinction to naturally occurring sterols, it was found, when studying the reaction of sterol derivatives, that the production of an immediate red colour (band at $500\mu\mu$) with either of the reagents, is specific for the $\Delta^{1,2}$ (or $\Delta^{1,13}$) linkage of the sterol ring system. It is suggested that the primary reaction in all sterol colour reactions consists in the shifting of the double linkage into the $C_{1,2}$ (or $C_{1,13}$) position, and the subsequent formation of coloured carbonium salts. Thus the primary red phase of the ergosterol reaction appears to be due to the presence of the $\Delta^{1,2}$ linkage. Heilbron, Morton and Sexton (*J. Chem. Soc.*, 1928, 47) inferred "that of the three double bonds in ergosterol, two occupy the same position as in cholesterolene." Since cholesterolene gives the red reaction but not the blue, the final blue stage of the ergosterol reaction may justifiably be ascribed to the influence of the third double linkage, the position of which is at present unknown.

P. H. P.

Vitamin Content of Honey. E. Hoyle. (*Biochem. J.*, 1929, 23, 54-60.)—

The experiments recorded in the literature suggest that honey is not a good source of vitamins. However, since these tests were made, vitamin research has progressed considerably, and it therefore seemed advisable to test honey by the more refined methods now available. Two representative samples, one a fresh English comb honey and the other a West Indian granular honey, were obtained for the purpose, and tested, and both were found to be deficient in vitamins *A*, *B*₁, *B*₂, *C* and *D*. Tables and curves show the results. Therefore, as shown by other workers, honey is not a source for these vitamins, and this deficiency is not due to deterioration consequent on treatment or storage.

P. H. P.

Vitamin D and Resistance of Chickens to Parasitism. J. E. Eckert and L. A. Spindler. (*Amer. J. Hyg.*, 1929, 9, 292.)—The four experiments given were designed to show whether the power of resistance of chickens to nematode worms (*Ascaridia lineata*, Schneider) was decreased by the absence of vitamin *D* in their diet. The criteria, whether the resistance to parasites was lowered, were the number and length of the worms in the intestines of the chickens at the end of the experiments (3 weeks after being infected with parasites). In the first experiment, the 10 chickens fed on vitamin *D*-deficient diet, failed to develop

rickets (judged by absence of leg weakness) apparently because of the inclusion of potassium phosphate in the salt mixture used in the diet. Resistance was not lowered. In the second experiment (potassium phosphate excluded) leg weakness developed in the minus *D* group on the 12th day. The minus *D* group and the plus *D* group were infected with parasites four days later. Resistance was again not lowered. In the third experiment neither group was infected till the birds were 72 days old, thus allowing more power of resistance to develop in the plus *D* group. In this experiment, in which cod-liver oil was the source of the vitamin, the average number and size of the worms in the minus *D* group showed a lowering of resistance, but this might be attributed to the presence of vitamin *A* in the cod-liver oil. In the fourth experiment vitamin *D* was supplied by daily exposure to a mercury vapour lamp. Judged by the number and size of the worms, resistance was not lowered, though, judged by the rate of growth, the effects of the parasites were more severe in the minus *D* group, indicating that vitamin *D* is a factor in protecting chickens against the effects of this nematode.

R. F. I.

Bacteriological.

Bactericidal Action of the Nitroso-Compounds. E. A. Cooper and R. B. Haines. (*Biochem. J.*, 1929, 23, 10-16.)—The nitrosoanilines are more effective germicides than the corresponding nitrosophenols. Nitrosoaniline will inhibit bacteria in concentrations of 1 in 100,000, but nitrosophenol is inhibitory in concentrations of not lower than 1 in 20,000. Both types of compounds show their high germicidal power only in long period bactericidal tests. A study has now been made of (1) the possible application of the nitrosoanilines as internal disinfectants, and (2) the mechanism of their bactericidal activity. The results show that an essential condition for the bactericidal action of the nitrosoanilines is the maintenance of the aminonitrogen in the tervalent state. The hydrochloride and methiodide are weak germicides. Nitrosoaniline and nitrosodimethylaniline are slightly soluble in water. The inhibitory concentration of nitrosodimethylaniline (*B. coli*, 48 hours at 37° C.) is 1 in 170,000. However, nitrosodimethylaniline is easily soluble in glycerol, propylamine, or formamide without significant loss in germicidal power, and the possibility of its clinical application is at present under investigation. The nitroso-compounds are slowly-acting disinfectants, and exert only a small bactericidal action in short periods, which increases greatly in intensity in periods of 24 to 48 hours. In order to study the mechanism of the action quantitative studies were carried out to ascertain the reactivity of the nitroso-compounds towards amino-acids, proteins, lipins and nucleic acids. They were found to have little or no action on amino-acids and proteins, but to react very gradually with nucleic acid, with the formation of a dark green insoluble product; this compound is possibly a salt of the nitroso-base with the nucleic acid. There is thus a distinct analogy in the case of nitroso-compounds between the process of germicidal action and the reactivity with nucleic acid, an essential constituent of cell nuclear material and associated with the mechanism of growth.

It is therefore concluded that the nitroso-compounds owe their slow germicidal action and marked inhibitory power to their gradual chemical interaction with the nuclear constituents of the cell, thus interfering with and retarding the biochemical mechanism of growth. The influence of concentration on the uptake of *p*-nitrosodimethylaniline by nucleic acid was studied by dialysis. P. H. P.

Biochemistry of Dry-Rot in Wood. E. C. Barton-Wright and J. G. Boswell. (*Biochem. J.*, 1929, 23, 110-114.)—The biochemical action of the saprophytic and parasitic fungi which cause decay of lignified tissues is little understood. Mycological literature usually states that the action of the fungal hyphae is to cause delignification of the lignocellulose complex by removal of the lignin, and to leave a residue of cellulose. These results have been mainly attained by the study, on sound and decayed wood, of microchemical tests only, which are of little value in this work. Owing to the conflicting evidence, which is discussed, given by previous workers, an investigation of wood attacked by *Merulius lachrymans* has been carried out with the use of modern methods of cellulose analysis. A study was made of the action of the fungus on completely decayed spruce-wood (*Picea excelsa*). Through the fungus the wood loses weight, and is converted into the so-called touch-wood, which powders easily, to give a brown dust. A comparison table of the analyses of the sound and decayed spruce-wood is given. Direct determinations of the cellulose and lignin in the decayed wood show decrease of the former and increase of the latter, and determination of the methoxyl groupings confirm the increase of the lignin. There is shown an increase of 57 per cent. of lignin, and a decrease of 60 per cent. of cellulose. Therefore there is no delignification of the wood by the fungus; the main attack is confined to the cellulose. The hexosans, mannan and galactan, are also removed, and it is suggested that *M. lachrymans* first attacks these two easily hydrolysed bodies, and then the cellulose. The fungus is very sensitive to the presence of acids; coniferous (soft) wood can be made resistant to *Merulius* by impregnation with tannic acid. The presence of acids produced by hydrolysis would hamper the fungus in its attack on the wood, and it may be on this account that the hemicelluloses are not affected. Therefore the effect of the fungus *Merulius lachrymans* (the cause of dry rot in wood) is to remove the galactan, mannan and cellulose fractions, whilst the hemicelluloses and lignin are not affected, *i.e.* no delignification of the woody tissues takes place. P. H. P.

Toxicological and Forensic.

Pharmacology and Toxicology of Tetrachlorethylene. P. D. Lamson, B. H. Robbins and C. B. Ward. (*Amer. J. Hyg.*, 1929, 9, 430.)—The absorption of tetrachlorethylene by the blood, lung and liver, its pathological effect, and its toxicity have been contrasted with those of chloroform and carbon tetrachloride. If normal dogs are given doses of tetrachlorethylene up to 10 c.c. per kilo. (50 times the therapeutic dose) no indication of absorption is to be observed. If larger doses are given, or if doses of 4 c.c. or more per kilo. are given in

cases where the intestine contains fat, absorption will be observed in all cases, though the degree of absorption varies greatly with the species of animal. Alcohol or low calcium balance greatly increases the toxicity of carbon tetrachloride, but out of 18 dogs treated with doses of from 4 to 15 c.c. of tetrachlorethylene per kilo., with 4 c.c. of alcohol per kilo., 15 recovered with no apparent functional or pathological disturbances. Dogs can be completely anaesthetised if they inhale tetrachlorethylene in concentrations of 62 mgrms. per litre. Since tetrachlorethylene has a much higher boiling point than carbon tetrachloride or chloroform, it was found impossible to cause surgical relaxation even after warming it, but with the cone method any degree of anaesthesia could be induced. If tetrachlorethylene is inhaled or injected intravenously in amounts, death may take place at once. Dogs given doses up to 4 c.c. per kilo. at intervals of 2 or 3 days for several months show no pathological changes in the liver; this contrasts very favourably with the widespread destruction of liver tissue brought about by carbon tetrachloride. Chloroform causes functional disturbance of both liver and kidney. The precautions necessary in giving carbon tetrachloride are unnecessary in giving tetrachlorethylene, although it is suggested that they be observed until this new drug has been more extensively used on man. The experiments indicate that tetrachlorethylene could be used in the treatment of hookworm disease with far greater safety than either oil of chenopodium or carbon tetrachloride.

R. F. I.

Cellular Toxicity of Gaseous and Volatile Poisons. (Mme.) S. Lallemand. (*J. Pharm. Chim.*, 1929, 9, 380-390.)—Exposure of freshly-laid eggs to the action of different gases and vapours in a closed vessel for various periods shows that the eggs develop normally on subsequent incubation after remaining for 8 days in hydrogen, nitrogen, oxygen, or carbon monoxide, which are, therefore, fundamentally non-toxic. Nitrous oxide is slightly toxic, and coal gas more so (toxic time 6 days); then follow carbon dioxide (3 days), acetylene (2 days), chlorine (5 hours), sulphur dioxide and hydrogen chloride (2 hours), ammonia and hydrogen sulphide (3 minutes). The saturated vapours (at 18° C.) of nitric acid, naphthalene, turpentine oil, petrol, aniline, and camphor are not toxic, and those of nitrobenzene and phenol only slightly toxic. For other vapours the toxic times are: iodine 8 days; amyl nitrite 5 days; toluene, amyl alcohol, petroleum spirit, chloral hydrate, butyl alcohol, 4 days; carbon tetrachloride, propyl alcohol, bromoform, 2 days; benzene, 18 hours; ether, 10 hours; ethyl alcohol, 9 hours; methyl alcohol, 8 hours; formic acid, 7 hours; acetic acid, acetone, benzyl chloride, ethyl chloride, chloroform, 5 hours; ethyl iodide, 3 hours; ethyl bromide, 2 hours; carbon disulphide, bromine, 1 hour; nitrogen peroxide, 30 minutes.

T. H. P.

Effect of Nicotine upon White Mice. C. H. Thienes. (*Amer. J. Hyg.*, 1929, 9, 500.)—The effect of the common use of tobacco by adolescents upon their growth is unknown, and preliminary experiments on this point by injecting nicotine into growing white mice have been carried out. Although the effects of injected

nicotine may not be quite the same as in actual smoking, yet it is generally agreed that nicotine is one of the chief factors responsible for the effects of tobacco smoking. Thirty-two mice were fed on whole wheat flour, greens, milk, cod-liver oil and raw chopped beef. On the 7th to 10th day after birth fourteen test mice receive injections twice daily, in the loose areolar tissue between the scapulae, of nicotine base in 0.85 per cent. sodium chloride solution. Eighteen controls were injected with salt solution alone. The absolute dose was increased once or twice per week, according to the severity of the symptoms produced by the previous dose. In the first week the average dose was 0.3 micromgrms. per gm. of mouse, and in the eighth week 2.3 micromgrms. Non-fatal doses produced symptoms ranging from mild excitation to severe clonic and tetanic convulsions. The weight curve of the test mice was very close to that of the controls. There was a marked decrease in susceptibility to nicotine as the mice grew larger, considered to be due to the natural resistance of age, rather than to an acquired tolerance. In view of the fact that results different from the above have been reported on rabbits, further experiments on other species are required.

R. F. I.

Agricultural.

Determination of Organic Carbon in Soils. G. W. Robinson, W. McLean and R. Williams. (*J. Agric. Sci.*, 1929, 19, 315-324.)—The carbon is determined by the quantitative oxidation of the organic matter by sulphuric acid in a Kjeldahl apparatus to carbon dioxide, water, and sulphur dioxide, and the determination of the sulphur dioxide produced in the process. The sulphur dioxide is conveniently absorbed in a tower absorber with 0.5 *N* iodine, and, after aeration, the excess iodine is titrated with sodium thiosulphate. Sufficient soil to furnish 0.02 to 0.05 gm. of carbon is used and ground to pass a 100-mesh sieve, and 25 c.c. of sulphuric acid, 5 gm. of potassium sulphate and 0.3-0.4 gm. of copper sulphate are put in the Kjeldahl flask. This method gives results which average 89.6 ± 1.03 per cent. of the combustion figures, so that it is proposed that the percentage of carbon calculated from the sulphur dioxide should be multiplied by the factor 1.116. The method is applicable to carbonate soils without correction for inorganic carbon, and nitrogen can conveniently be determined on the same sample in one series of operations. It is suggested from data with certain peats that the factor 1.724 for converting organic carbon to organic matter is low, and that a fair approximation would be obtained for most purposes by multiplying by 2.

D. G. H.

The Pyrogallol Method for the Determination of Nitrates in Soil and Waters. L. U. De Nardo. (*Giorn. Chim. Ind. Appl.*, 1929, 11, 107-109.)—Nitrates in the small proportions in which they occur in soils or natural waters may be determined by means of their reaction with either pyrogallol or pyrogallol-sulphonic acid. The latter reagent is prepared by dissolving 5 grms. of pyrogallol in 10 c.c. of concentrated sulphuric acid, heating the solution for a few moments

at 80–90° C., allowing the acid formed to crystallise, and dissolving in water to 200 c.c. One hundred grams of the soil, recently sampled, are shaken for 6 hours with 200 c.c. of water, and then filtered through a folded paper. Of the filtrate, 80 c.c. are shaken in a tared flask with 1–3 c.c. of cold saturated aqueous baryta, the liquid being then heated to the boiling point, allowed to stand so that the precipitate settles, and treated with 0.5–1 c.c. of 50 per cent. basic lead acetate solution. After 2 or 3 minutes the excess of lead and barium is precipitated by about 5 c.c. of saturated sodium sulphate solution, the volume being made up to 100 c.c. with water when cold, mixed, and passed through a dry filter. Ten c.c. of the filtrate are transferred to a 50 c.c. flat-bottomed porcelain capsule. If the soil contains more than 0.1 mgrm. of nitrite as N_2O_3 per kilo., this is removed by adding to the 10 c.c. a drop of concentrated urea solution and, with stirring, about 1 c.c. of concentrated sulphuric acid. After 10 minutes the liquid is treated with 0.5 c.c. of the 2.5 per cent. pyrogallolsulphonic acid solution and, slowly and with stirring, with 20 c.c. of concentrated sulphuric acid. After the lapse of an hour the colour developed is compared with the colours obtained under identical conditions with solutions of known nitrate contents.

If this determination indicates more than 0.1 mgrm. of KNO_3 (per 4 grms. of soil), the test should be repeated as follows: Five c.c. of the solution, defecated as above, are treated in the porcelain dish with urea and sulphuric acid, and afterwards with 0.5 c.c. of a solution containing 2.5 grms. of pyrogallol and 0.1 gm. of sodium bisulphite per 100 c.c., and, with stirring, with 25 c.c. of concentrated sulphuric acid. As before, the colour comparison is made after one hour.

If negative results are given by the above tests, the defecated alkaline solution may be concentrated in order that smaller proportions of nitrate may be sought. With suitable modifications the method may be applied to aqueous vegetable extracts, foodstuffs, etc.

T. H. P.

Organic Analysis.

Use of Ozone for the Determination of the Constitution of Unsaturated Compounds. J. Doeuvre. (*Bull. Soc. Chim.*, 1929, 45, 140–152.)—The methylene grouping $\text{CH}_2\text{:C}(\text{CH}_3)\text{.CH}_3$ and the isopropylidene grouping, $\text{CH}_3\text{C}(\text{CH}_3)\text{:CH.}$, in unsaturated compounds of the terpene series, may be determined by subjecting the compounds to the action of ozone, decomposing the resulting products with water, and determining, in the former case, the formaldehyde, formic acid, and carbon dioxide, and in the latter, the acetone formed. In this way the proportions of the two isomerides in a mixture may be ascertained. From 0.01 to 0.02 gm.-mol. of the substance, dissolved in 8 or 10 c.c. of acetic acid mixed with 2 c.c. of recently-boiled distilled water, is placed in the first of four bubbling apparatus, of about 80 c.c. capacity, these being entirely of glass and provided at the ends with cups to make mercury seals. Each of the three other bubblers contains 15–20 c.c. of water to retain the products formed, and in certain cases a fifth, charged with standard baryta solution, is added to absorb carbon dioxide, which is, however,

never formed in appreciable quantity. The bubblers are cooled with ice and an oxygen-ozone mixture is passed through the whole apparatus, the gas stream being stopped 30 minutes after the issuing gas begins to smell strongly of ozone. The contents of all the bubblers, with rinsings, are transferred to a 100 c.c. flask, which is left at the ordinary temperature for 12 hours before analysis.

The formaldehyde is determined colorimetrically with the Grosse-Bohle reagent, prepared by dissolving 1 gm. of rosaniline hydrochloride in 500 c.c. of water, adding a solution of 25 grms. of crystallised sodium sulphite and 15 c.c. of hydrochloric acid (1·12), making up to a litre, and filtering after one or two days. Measured quantities of the hydrolysed solution of the ozonised material are diluted to about 5 c.c. in similar test-tubes, treated with 1·5 c.c. of hydrochloric acid (1·12) and 3 c.c. of the reagent, made up to 10 c.c., and compared after 12 hours with similar tubes containing known proportions of formaldehyde. The results are accurate to within 5 or 10 per cent.

The formic acid is determined by boiling with red mercuric oxide and absorbing the carbon dioxide formed in standard baryta solution. A wide-necked flask of about 80 c.c. capacity is fitted with an air-supply tube reaching almost to the bottom of the flask, and with two absorption apparatus containing about four times the estimated volume of baryta. Sufficient of the solution to give carbon dioxide corresponding with about 10 c.c. of 0·1 *N* baryta is mixed in the flask with slight excess of aqueous sulphur dioxide for 5 minutes, after which about 8 grms. of red mercuric oxide are added, and the flask closed and shaken. When sulphur dioxide is no longer perceptible, the liquid is heated to boiling and kept gently boiling for 10 minutes, the carbon dioxide formed being then expelled by a current of air, free from the dioxide, passing for 15 minutes; a gentle current of air may be passed also during the heating.

To determine the acetone, an aliquot part of the hydrolysed liquid, after removal of the aldehyde and formic acid, is distilled slowly through a column, the condenser tube dipping below the surface of water in a flask cooled in ice-water. The acetone is often accompanied by aldehydic or ketonic substances, which may be destroyed by a second distillation with permanganate in presence of acetic acid, but this treatment also oxidises the acetone to some extent; with 0·01, 0·0057, and 0·0044 gm.-mol. of acetone the losses are 5, 8·8 and 9·6 per cent. respectively. The acetone is finally determined by Messinger's method. When this method is applied to eugenol, secondary transformations occur which vitiate the results.

T. H. P.

Microchemical Distinctions of Essential Oils. L. Rosenthaler. (*Amer. J. Pharm.*, 1929, **101**, 191-196.)—In the following microchemical reactions with essential oils the reagents used are as follows:—A. *p*-Nitrophenylhydrazine, 0·5 gm., hydrochloric acid, 1 c.c., glacial acetic acid, 7 c.c., water to make 50 c.c.; B. Phenylhydrazine solution; C. Semicarbazide hydrochloride, 5 gm. potassium acetate, 5 gm., water, 15 c.c.; D. Saturated solution of potassium permanganate in acetone; E. Commercial solution of sodium acid sulphite; F. Thiery's reagent:

a solution of 0.5 grm. of phenolphthalein in 30 c.c. of alcohol mixed with water until turbidity appears, when 20 grms. of sodium hydroxide are added and aluminium powder in small portions. After decolorisation the liquid is made up to 150 c.c. with boiled water.

Bitter almond oil.—A: deep orange red needles; B: needles and rods; C: a variety of forms, rods, plates (the latter often with crenated edges), knife-blade and saw-tooth forms, sometimes scissor-like; D: warmed with a drop of hydrochloric acid, crystals of benzoic acid appear; E: a great variety of forms, needles prisms, square plates, etc.; F: red tint.

Anise oil.—A: orange rods; C: colourless prisms with plates and other forms; D: the reagent with hydrochloric acid. Rods of anisic acid appear.

Cajuput oil.—A 5 per cent. hydroquinone solution produces, after vigorous stirring, colourless prisms and other forms; stirring with potassium iodide and iodine solution produces a pasty mass, but if the reagent and oil are cautiously placed in contact, grey, green or violet tree-like forms appear; potassium bromide-bromine solution produces yellow masses, referable to cineole (eucalyptol).

Clove oil.—Concentrated aqueous and alcoholic alkalis produce precipitates due to eugenol; also, ammonia vapour produces a mass of crystalline crystals, and the oil stirred with a drop of piperazine solution gives a crystalline reddish mass of plates.

Cinnamon oil.—A: orange-red undefined crystalline precipitate. This is a reaction for the aldehyde, as are the following:—C: rods, single or in groups; F: rods and needles grouped or separate. Solution of benzidine in glacial acetic acid: Yellow precipitate which may grow into groups of needles. With permanganate, crystals of cinnamic acid are formed, and with a concentrated aqueous solution of *m*-phenylene-diamine hydrochloride, orange-crystals at first and then needles; and with the *p*-hydrochloride dark orange granules, then groups of needles.

Citrus oil.—A: orange granules; C: slowly small rods, partly in groups.

Eucalyptus oil.—The reactions of cineole as noted under cajuput oil, but stronger.

Fennel oil.—A: abundant orange needles; C: numerous crystalline and amorphous forms, a right-angled crystal and rods in saltire and groups. Oxidation gives results similar to those with anise oil.

Cherry laurel.—Similar reactions to bitter almond oil.

Oil of pulegone.—A: numerous fine dendritic orange-red forms, probably derived from pulegone.

Oil of saffras.—Oxidised with D. and sublimed on an asbestos plate after removal of the acetone, the sublimate will contain piperonal (from saffrole). The odour, as well as the orange-red needles with reagent A, are distinctive.

Mustard oil.—Colourless rods and prisms with 50 per cent. piperazine solution; with bromine water or potassium bromide and bromine solution, amorphous yellow precipitate; ammonium silver nitrate gives silver sulphide.

Oil of thyme.—A drop mixed with sodium hydroxide solution, then with a concentrated potassium iodide and iodine solution produces in the cold, or on slightly warming, a red precipitate of dithymol di-iodide. If a drop of thyme oil is added to a mixture of zinc chloride and phthalic anhydride, and the mixture melted in a small test tube, a red mass will be formed. On cooling, if water is added and then excess of sodium hydroxide solution, a blue liquid is produced. (phthalein reaction.) The result is due to thymol. Illustrations of many of the crystals are given. D. G. H.

Identification of Rayon (Artificial Silk). W. D. Grier. (*Ind. Eng. Chem.*, 1929, 21, 168–172.)—Microscopical examination of the fibres, and particularly of their cross-section, affords a reliable means of distinguishing between the four general types of artificial silk now on the market, namely, viscose, cuprammonium, nitro, and acetate silks. The first three also polarise brilliantly, acetate silk only feebly. As regards chemical tests, nitro silk gives a very distinct reaction with diphenylamine and sulphuric acid reagent, and viscose may be detected by a test proposed by Schreiber and Hamm, which depends on the formation of minute residual amounts of sulphur compounds when the material is heated on a steam-bath with very dilute sulphuric acid. Acetate silk dissolves readily in acetone. W. P. S.

English Bookbinding Leathers. R. W. Frey, L. R. Leinbach and E. O. Reed. (*J. Amer. Leather Chem. Assoc.*, 1929, 24, 190.)—Twenty-three whole skins tanned and dressed by English tanners for book-binding purposes have been examined physically and chemically. The physical measurements include those of stretch, tensile strength and weight per unit area. The chemical determinations include the percentages of mineral acid, grease and water-soluble matter, also the degree of tannage (parts of fixed tan per 100 parts of hide substance), and whether the tan was of the pyrogallol or the catechol type. The tensile strength varied in 13 goat skins from under 2000 to over 3000 lbs. per sq. in. ; in 6 calf skins from under 2000 to over 3500 lbs. All the leathers labelled as being free from mineral acids contained less than 0.3 per cent. of acid (as sulphuric acid), as determined by the Procter-Searle method. In those not guaranteed, the acid as sulphuric acid varied from 0 to 2.2 per cent., the latter giving a water extract of P_H value 2.4. Five of the leathers had a figure, for the degree of tannage, of 70 or more, seven 60 to 70, three 55 to 60, and seven less than 55. It is stated that too high a figure results in a tax on the life of the fibre when the leather is submitted to repeated bending. Fifteen of the leathers, mostly goat skins, contained under 3 per cent. of matter soluble in petroleum spirit, the highest figure being 11.1. Too low a grease content is said to be one of the causes of deterioration of leather book-bindings.

(*Abstractor's Note.*—No conclusions as to the relation of these data to the life of the leathers can be drawn until books bound with these leathers have been submitted to conditions of atmosphere and light for 15 to 20 years.) R. F. I.

Quantitative Analysis of Tin in Organic Compounds. H. Gilman and W. B. King. (*J. Amer. Chem. Soc.*, 1929, 51, 1213–1215.)—A slight excess of an approximately 4 per cent. solution of bromine in carbon tetrachloride is added to 0.5 gm. of sample in a cooled, tared 60 c.c. porcelain crucible, and is followed by 2 c.c. of a mixture of concentrated nitric and sulphuric acids (1:6). After the violent reaction has ceased, 4 c.c. of a 1:1 mixture of the acids are added, then 2 c.c. of nitric acid, and finally 5 c.c. of fuming nitric acid. After 30 minutes on the steam bath the oxides of nitrogen, the carbon tetrachloride, and finally the sulphuric acid, are removed at a low heat, and the greyish residue ignited till constant in weight and weighed as stannic oxide. The maximum recorded error for a number of organo-tin compounds is about 0.5 per cent. J. G.

Inorganic Analysis.

Determination of Hydrogen Ion Concentration by a Modified Colorimetric Method. D. H. Cameron. (*J. Amer. Leather Chem. Assoc.*, 1929, 24, 76.)—This method was devised to overcome inaccuracies arising from the fact that the standard colour tubes are not permanent, that the indicator solutions are not stable, and that varying shades of colour may develop in a series of tubes using the same indicator at the same P_H . The procedure eliminates the need of prepared colour standards. The approximate P_H of the unknown solution is first determined. Two 50 c.c. Nessler cylinders of uniform diameter are taken. Into one are put 25 c.c. of the unknown solution with a volume of diluted indicator measured by a small pipette. Into the other cylinder are introduced 25 c.c. of the necessary buffer solution (one of the three given below) with the same volume of the same diluted indicator; 0.2 *N* sodium hydroxide (free from carbonate) is added till the colours in both cylinders are the same after an equal volume of water has been added to the unknown solution. The volume of sodium hydroxide required is noted, and from a curve or table based on Clark's figures the P_H value can be deduced. The three standard buffer solutions given are 0.1 *M* potassium hydrogen phthalate for the range 4.0 to 5.8, 0.1 *M* potassium dihydrogen phosphate for the range 5.8 to 7.8, and 0.1 *M* boric acid for the range 7.8 to 10.0.

P_H values below 4.0 may be obtained by using potassium hydrogen phthalate and adding 0.2 *N* hydrochloric acid. The method works well where there is no scarcity of sample and where the test solution is colourless. Tables for the range 4.0 to 10.0 are given. R. F. I.

Potentiometric Titration of Ammonia. E. B. R. Prideaux. (*J. Soc. Chem. Ind.*, 1929, 48, 87–88T.)—Although ammonia cannot be titrated with the hydrogen electrode, it may be back-titrated if the cell-combination Pt, | quinone, quinhydrone, HCl, NH_4Cl | saturated KCl | saturated calomel electrode, is used. Ammoniacal gas liquor (20 c.c. of an approximately 0.1 *N* solution) was pipetted into an excess of 0.1 *N* hydrochloric acid, boiled for an hour to remove volatile acids, cooled, the quinone-quinhydrone added, and the excess of acid determined

potentiometrically with 0.1 *N* alkali. The potentials (*E*) of the theoretical end-points may be determined for different concentrations (*c*) of ammonium chloride from the equations $E = 0.453 - 0.058 \log [H^+]$ and $P_H = 4.685 - 0.5 \log c$, *E* being 141, 137 and 132 millivolts when *c* is 0.04, 0.03 and 0.02, respectively. The accuracy of the titration is that obtainable with the weight burette. The method is therefore preferable to titration with methyl red indicator, especially since it may be used with coloured or turbid solutions, and provides a warning of the approach of the end-point. J. G.

Determination of Tin by Rapid Electrolysis. J. Švéda and R. Uzel. (*Collection des Trav. Chim. Czechoslovaq.*, 1929, 1, 203-222.)—Stannous or stannic tin (0.5 to 0.05 gm.) may be deposited from 200 c.c. of solution in the presence of 10 grms. of ammonium oxalate, 5 grms. of oxalic acid and 2 grms. of hydroxylamine hydrochloride (or 4.724 grms. of sulphate) by electrolysis for 25 minutes at 60 to 70° C. with a current density of 5 amps. at a voltage of 2.5 to 3.5 volts. The solution, which has been well stirred, is maintained at 65° C. by the current, and is finally washed out with a large volume of water without interrupting the current. The deposit is bright and adherent, and an accuracy of ± 0.32 per cent. is obtainable for from 0.1 to 0.5 gm. of tin. Deposits of stannous tin from neutral solutions were powdery, whilst the deposition of stannic tin from alkaline solutions was too slow. The electrodes were of platinum-iridium wire gauze, the cathode being copper-plated. For deposition of tin from ammonium thiostannate solutions the copper-plated cathode was also tin-plated. In this case electrolysis was slow, but gave satisfactory, though slightly high, results in the presence of 30 c.c. of a 40 per cent. solution of sodium sulphite as depolariser for polysulphide ions. The hydroxyl ion concentration was maintained below a certain limit by the addition of 3 to 6 grms. of an ammonium salt of a strong acid. Satisfactory results were also obtained with 200 c.c. of electrolyte containing 10 c.c. of hydrochloric acid and 2 grms. of hydroxylamine hydrochloride. With more than 0.5 gm. of tin the deposit is improved by the addition of 0.4 gm. of ammonium persulphate, in addition to the hydroxylamine salt. Hydrazine salts produce coarse, crystalline deposits. J. G.

Confirmatory Test for Aluminium. R. Gemmill, R. Brackett and C. R. McCrosky. (*J. Amer. Chem. Soc.*, 1929, 51, 1165.)—A piece of pure asbestos fibre, half the size of a pea, is impregnated with 0.05 *N* cobalt nitrate solution and ignited on a platinum wire. It is then dipped in a solution of the aluminium hydroxide precipitate in the minimum amount of nitric acid and re-ignited. The test (formation of a blue residue) is sensitive to 0.2 mgrm. of aluminium or 0.5 mgrm. of zinc, and is unaffected by sodium (*cf.* Pañganiban and Soliven, *ANALYST*, 1928, 53, 616). J. G.

Analytical Chemistry of Beryllium. Part II. L. Moser and F. List. (*Monatsh. Chem.*, 1929, 51, 1133-1141.)—Beryllium cannot be separated from the alkaline earths by ammonia, even that free from carbonate; on the other hand,

hydrolytic precipitation with ammonium nitrite and methyl alcohol (Part I, ANALYST, 1928, 53, 402) provides an efficient separation from *strontium*, *calcium* and *magnesium*. *Barium* is best separated as sulphate, the precipitation being effected gradually; the beryllium in the filtrate is precipitated by tannin. The nitrite method can also be used successfully for the separation from *zinc*, *cadmium*, *nickel*, *cobalt*, *manganese*, and *thallium*. Zinc and cadmium may also be precipitated by hydrogen sulphide, manganese by ammonium persulphate, from feebly acid sulphate solution. Thallium is precipitated as chromate in the concentrated filtrate from the beryllium precipitation (ANALYST, 1928, 459), and, if the solution to be hydrolysed with ammonium nitrite is acid, it must be neutralised with sodium carbonate, not ammonia, as thallos chromate is slightly soluble in presence of ammonium chloride.

Arsenic and *antimony* may be separated from beryllium by hydrogen sulphide precipitation in hydrochloric acid of such concentration as to yield precipitates free from adsorbed beryllium: the black, crystalline modification of antimony trisulphide can be obtained by known means. The separation of *tin* by hydrogen sulphide fails by reason of beryllium adsorption in the stannic sulphide. The following method is given: the strongly acid, boiling chloride solution is treated with 5 c.c. of 10 per cent. tannin solution, and 10 to 20 grms. each of ammonium acetate and nitrate. The boiling solution becomes turbid, and the precipitate gradually flocculates; flocculation of the tin adsorption complex is complete after one hour's heating on the water-bath. The precipitate is collected and washed with hot ammonium acetate solution containing a little tannin. If more than 0.2 gm. of tin is present, the precipitate is dissolved in hot, strong hydrochloric acid, and the operation repeated. After being dried, the precipitate is ignited gradually, finally on a blast burner, and weighed as SnO_2 . The combined filtrates are evaporated, neutralised with ammonia, and the beryllium precipitated with tannin.

For the systematic separation of beryllium from a solution containing other metals, the acid solution is first precipitated with hydrogen sulphide; the filtrate is oxidised with bromine, the excess of which is boiled off. Barium, if present, is removed next as sulphate; the trivalent and quadrivalent metals, together with the beryllium, are then precipitated by nitrite hydrolysis. The precipitate is dissolved in nitric acid, and all the metals present, with the exception of beryllium, precipitated by tannin from acetate solution: the filtrate is made ammoniacal and treated with more tannin, whereby the beryllia is isolated. W. R. S.

Analytical Chemistry of Gallium. (Part II.) L. Moser and A. Brukl. (*Monatsh. Chem.*, 1929, 51, 73–81.) (Part I, ANALYST, 1929, 64.)—So far, no satisfactory methods for the quantitative separation of gallium from metals of the ammonia group are known. The authors show that a number of satisfactory separations can be effected by means of cupferron. *From aluminium, chromium, indium, uranium, cerium*: the chloride or sulphate solution (0.01 to 0.3 gm. Ga), which may contain ammonium salts, is adjusted with 2 *N* sulphuric acid to a

bulk of 200 to 300 c.c., and treated in the cold with 0.1 grm. of cupferron in 6 per cent. solution; a white flocculent precipitate is obtained, which clots together above 30° C., and can then be crushed with a glass rod to a crystalline mass; it is collected on paper with the help of gentle suction. The first filtrate, which is always cloudy, is re-treated with 1 to 2 c.c. of reagent, and again passed through the same filter. If now it remains clear after an hour's standing, the precipitation may be considered complete; if not, the re-treatment must be repeated. The precipitate is washed with 2 *N* sulphuric acid; it must be strictly free from chlorides as gallia can be volatilised completely by heating with ammonium chloride. The precipitate is gently, then strongly, ignited in a porcelain crucible, and weighed as Ga_2O_3 , which is hygroscopic. Double precipitation is necessary if the quantity of aluminium present exceeds 2 grms. In the separation from indium, the washing of the precipitate must be very thorough, and cupferron should be added to the acid wash-liquor. If indium predominates, the precipitation is repeated; a small quantity of india is detected by the yellow tint of the gallia during ignition. In the separation from uranium, care must be taken to prevent any reduction, as quadrivalent uranium is quantitatively precipitated by cupferron. *From iron.*—(a) For little gallium from much iron, the acid solution free from ammonium salts is almost neutralised with sodium carbonate, decolorised in the cold with an excess of sodium thiosulphate, and boiled for 15 minutes, 10 c.c. portions of aniline being added at 5-minute intervals, to depress the final acidity, and thereby complete the precipitation of the gallium hydroxide. The hot solution is filtered, the precipitate carefully washed with hot water, and ignited. It always contains a little iron, and is treated according to (b) after fusion with bisulphate. (b) Little gallium from little iron: the solution is treated with a moderate excess of 10 per cent. sulphosalicylic acid solution and enough ammonia to produce a clear, pale red solution, which is boiled and treated with hydrogen sulphide till cold. The ferrous sulphide is filtered off and washed as usual, the filtrate acidified with acetic acid, and boiled free of hydrogen sulphide; gallium is then precipitated by excess of ammonium acetate and tannin, as described in Part I. (c) Much gallium from little iron; the nearly neutral solution is slowly poured into hot ammonia, when ferric hydroxide is precipitated and soluble gallate formed. The iron precipitate containing adsorbed gallia is treated according to (b); the gallium solution is acidified with acetic acid and precipitated with tannin (Separation of iron by nitroso- β -naphthol, ANALYST, 1928, 53, 558.)

W. R. S.

Gravimetric Methods for Vanadium. L. Moser and O. Brandl. (*Monatsh. Chem.*, 1929, 51, 1121–1132.)—The precipitation of ammonium metavanadate and mercurous vanadate was re-investigated; two new forms of weighing—silver orthovanadate and lead pyrovanadate—are described. *Ammonium metavanadate* was precipitated substantially as in Gooch and Gilbert's process, the alkali metavanadate solution being treated with an equal volume of cold-saturated ammonium chloride solution and a few drops of ammonia, and the liquid evaporated on the water-bath to the original bulk. The precipitate is

collected after 12 hours' standing in the cold, and washed with a minimum of saturated ammonium chloride solution; it is dried at 110°C. , and separated from the filter. This is first heated in a covered platinum crucible to 150°C. for the removal of the ammonium salt, then gradually to a higher temperature with the lid off. When the paper has been burnt off, the added precipitate is heated with the same precautions, as otherwise the ammonium chloride causes volatilisation losses. The molten pentoxide is made to run in a thin layer round the sides of the crucible during ignition at red heat; any lower oxides are thus re-oxidised. An improved *mercurous vanadate* precipitation method is described; the boiling alkali vanadate solution, which may contain a little nitric acid but no ammonium salts, is treated with 3 c.c. of 10 per cent. hydrogen peroxide and a large excess of mercurous nitrate solution (the powdered salt treated with hot water): 0.1 gm. V_2O_5 requires 40, 0.2 gm. 60 c.c. of this solution. For the destruction of the hydrogen peroxide the covered beaker is boiled half an hour; the precipitate is collected, washed with cold water, dried and separated from the filter, the paper ashed separately, and the precipitate strongly ignited to V_2O_5 . If this method is followed, the precipitate consists of sparingly acid-soluble pyro- and orthovanadate, whilst without hydrogen peroxide the more soluble hexavanadate $\text{Hg}_4\text{V}_6\text{O}_{17}$ is obtained. *Silver orthovanadate* is obtained from an alkali vanadate (maximum 0.2 gm.) solution (200 c.c. bulk) treated with 3 grms. of pure sodium acetate, 0.5 c.c. of strong ammonia, and an excess of silver nitrate. The liquid is boiled and transferred to the water-bath; after half-an-hour it is tested with a little more silver nitrate, and in case of a turbidity the liquid is boiled till clear. The dense, brown precipitate, Ag_3VO_4 , settles well; it is collected in a porous porcelain crucible, washed with hot water, dried at 110°C. , and ignited gently with the crucible placed inside a larger one. If the vanadate solution is alkaline it is boiled and treated, drop by drop, with nitric acid till permanently yellow; a few drops of ammonia are then added to decolorisation. If acid, the vanadate solution is neutralised with caustic soda. The determination as *lead pyrovanadate* is more tedious than the preceding, though the results are satisfactory.

W. R. S.

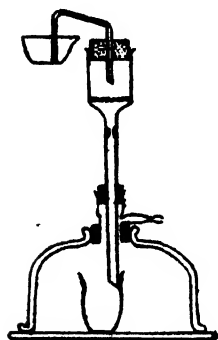
Reagent for Potassium, Ammonium, Rubidium and Caesium Ions.

T. G. Y. Arnal. (*Chim. et Ind.*, 1928, Oct.; *Ann. Chim. Anal.*, 1929, 11, 10-11.)—No precipitate results on the addition of 5 per cent. uranyl nitrate solution to a solution of sodium chromate (about 5 per cent. CrO_4), or to a solution of similar concentration of ammonium chromate, but in the latter case a precipitate forms on warming, and with a similar potassium chromate solution a precipitate forms in the cold. The precipitates are soluble in concentrated solutions of sodium chloride and more soluble in solutions of uranyl nitrate and in acids, and are but little soluble in alcohol. Thus if a uranyl nitrate solution is added to one of sodium chromate, so that there is a stoichiometric formation of uranyl chromate, a yellow precipitate will be formed on addition of potassium. Similarly, rubidium and caesium ions may be detected.

D. G. H.

Influence of Lithium, Rubidium, Caesium, and Magnesium upon the Detection of Potassium by Zirconium Sulphate. R. D. Reed and J. R. Withrow. (*J. Amer. Chem. Soc.*, 1929, **51**, 1062–1065.)—The authors' reagent (*ANALYST*, 1928, **53**, 456) will detect 1.0 mgrm. or more of potassium in 2 c.c. of reaction mixture in the presence of 50 mgrms. of lithium, 16.6 mgrms. of rubidium or of 11.6 mgrms. of caesium sulphate. It will detect 0.5 mgrm. or more in the presence of 50 mgrms. of magnesium sulphate, but not if 11.6 mgrms. of caesium sulphate are present. In such cases a blank test should always be carried out. Comparison with other reagents (sodium cobaltinitrite, chloroplatinic acid, and perchloric acid) showed that zirconium sulphate alone is a selective reagent for potassium in the presence of the fifth-group elements. J. G.

Separation of Lithium from Potassium, Sodium and Magnesium. L. Moser and K. Schutt. (*Monatsh. Chem.*, 1929, **51**, 975–994.)—The accuracy of the published methods was tested, with results given below. *Separation from sodium and potassium.*—The only serviceable methods are those based on the solubility of lithium salts in certain organic solvents; the chlorides of sodium and potassium are too soluble in strong hydrochloric acid for a quantitative separation. Extraction of the mixed chlorides with pyridine, commercial or anhydrous, gives low values for lithium, which can always be detected in the insoluble residue. The method of Winkler (extraction of the chlorides with absolute isobutyl alcohol) was followed with very slight modifications, and proved to give excellent results. Greater care was taken to ensure the complete dehydration of the alcohol, *i.e.* by three hours' boiling under a reflux condenser with barium oxide and distillation. The two principal changes effected were: (1) The substitution of a sintered glass crucible for a filter paper, as it was ascertained that the paper adsorbs appreciable amounts of lithium salt; (2) syphoning of the lithium extract on to the porous glass crucible instead of pouring the liquid out of the basin. This mode of working obviates the losses due to creeping of the solvent over the edge of the containing vessel. The syphon is worked by suction, its descending member passing through a stopper at the top of a filtration crucible of special construction (see diagram). A deduction of 0.0005 grm. is made from the weight of Li_2SO_4 found: this amount is added to the weight of $\text{K}_2\text{SO}_4 + \text{Na}_2\text{SO}_4$. Smith and Ross's method (*ANALYST*, 1925, 307)—separation of sodium and lithium perchlorates from the potassium salt by a 1:1 mixture of ethyl acetate and *n*-



butyl alcohol and subsequent action of a 20 per cent. solution of hydrogen chloride in *n*-butyl alcohol on the soluble perchlorates, sodium chloride being precipitated—was found to give low lithium results; all the sodium fractions gave strong lithium lines. *Separation from magnesium.*—Conversion of magnesium chloride into the oxide by double evaporation of the solution with yellow mercuric oxide (Berzelius) does not give chlorine-free magnesium oxide. The precipitation of

magnesium chloride solutions with alcoholic ammonium carbonate, though quantitative, gave high magnesium results, due to the adsorption of lithia by the magnesium ammonium carbonate, even after double precipitation. The only process of separation that gives correct results is Berg's *o*-hydroxyquinoline method (ANALYST, 1927, 52, 431). The solution of the chlorides, containing ammonium chloride (80 to 150 c.c. bulk), is precipitated at 70° C. with a 2 to 5 per cent. alcoholic solution of the reagent till the solution is yellow, the liquid being meanwhile heated to boiling. After cooling, the precipitate is collected on a porous glass crucible, well washed with hot water containing a little ammonia, and dried at 105° C. The filtrate is evaporated in a platinum basin, the residue dissolved in a little dilute hydrochloric acid, and the solution filtered into a tared platinum crucible; the lithium is determined in the usual manner as sulphate. If potassium and sodium are also present, the filtrate from the magnesium precipitate is evaporated to dryness, the residue gently heated for the removal of the ammonium salts, and the lithium in the fixed residue separated from potassium and sodium by isobutyl alcohol.

W. R. S.

Ceric Sulphate in Volumetric Analysis. V. Potentiometric Study of the Reaction between Ferrocyanide and Ceric Ions. N. H. Furman and O. M. Evans. (*J. Amer. Chem. Soc.*, 1929, 51, 1128–1133.)—The reaction $\text{Ce}^{++++} + \text{Fe}(\text{CN})_6^{-----} \rightleftharpoons \text{Ce}^{+++} + \text{Fe}(\text{CN})_6^{----}$ proceeds quantitatively from left to right in acid, and from right to left in alkaline solution, and the end-point may be accurately determined by Furman's potentiometric method (ANALYST, 1928, 53, 302). A stable 4*N* ceric sulphate solution was prepared by dissolving commercial rare earth oxides containing 45 per cent. of CeO_2 in sulphuric acid, and was standardised potentiometrically against pure sodium oxalate in the presence of hydrochloric acid (*cf.* Willard and Young, *id.*, 404). The potassium ferrocyanide solution, which should be about 0.1 *N*, is titrated with the ceric sulphate solution at 25° C. in the presence of sulphuric acid not exceeding 5 *N* or hydrochloric acid 0.2 to 2 *N* in strength. If the acidity is too low a white precipitate is formed, and if too high the end-point is sluggish. At the end-point there is a potential jump of at least 0.2 volt per 0.05 c.c. of 0.1 *N* ceric solution, while the sharp disappearance of the green colour, due to ferric ferrocyanide produced from traces of ferric iron, when the last traces of ferrocyanide are oxidised, may be used as a visual end-point. The reverse titration is accurate only if the major portion of the reagent is added rapidly, and it is not recommended for general use.

J. G.

Micro-Titration of Iodides, in Absence or in Presence of Large Proportions of Nitrite. J. F. Reith. (*Rec. Trav. Chim. Pays-Bas*, 1929, 48, 386–390.)—Quantities of iodide ion as small as ($0.5\gamma = 0.005$ mgrm.) may be determined by the bromine and sulphuric acid method, which is carried out as follows: The iodide solution (not more than 1 c.c.) is pipetted into a 25 c.c. Erlenmeyer flask and is rendered acid by dropwise addition of 0.5 *N* sulphuric acid, the reaction being tested by streaking methyl-orange paper with a platinum wire; an excess of two

drops of the acid is added, the P_H value being then about 1.6. Three drops of saturated bromine water, sufficient water to give a total volume of 2 c.c., and a little powdered pumice (0.5–0.8 mm. size) are added, and the flask placed obliquely on a very hot sand-bath. The liquid is boiled for 45 seconds after a distinct stream of steam begins to issue and is then cooled. The subsequent titration is made in artificial light, such as that from a Phillips sunlight lamp, direct radiation from which is avoided. The liquid is treated with 0.1 c.c. of 5 per cent. potassium iodide solution and 3 drops of 0.5 per cent. starch solution, and titrated slowly with 0.001 *N* thiosulphate solution, which is allowed to flow out near the bottom of the flask, held obliquely, from a graduated pipette holding 0.1 or 0.3 c.c. and reading to 0.001 c.c. Towards the end-point, 0.002 c.c. quantities of the solution are run in, comparison of the colour before and after mixing the liquid being made. One c.c. of 0.001 *N* thiosulphate corresponds with 21.15 γ of iodide-ion, and the correction for the sensitiveness of the starch-iodine reaction is $v \times 0.1$ mgrm. of iodine at 15–18° C., v being the volume of the liquid after completion of the titration. For quantities between 0.5 and 1.5 γ of iodide-ion, this method gives results accurate to less than 5 per cent., and for 1.5–10 γ , less than 2 per cent.

If nitrite is present, its disturbing influence may be avoided by the following azide method. The solution (at most 1 c.c.) is treated in the Erlenmeyer flask with excess of 5 per cent. sodium azide solution (1 mgrm. of HNO_2 requires 1.7 mgrm. NaN_3), and acidified with 2 *N* sulphuric acid, vigorous evolution of nitrogen and nitrous oxide occurring. If the odour of azoimide is not detectable, more azide solution must be added and the acid reaction of the liquid maintained. Two drops in excess of the acid and three drops of bromine water are added, the further procedure being that of the bromine-sulphuric acid method. T. H. P.

Physical Methods, Apparatus, etc.

Determination of Vapour Densities at Room Temperatures. E. F. Linhorst. (*J. Amer. Chem. Soc.*, 1929, 51, 1165–1167.)—Two 2-litre round-bottomed flasks connected by an oil manometer (60 cm. overall length, 5 mm. diameter) may be evacuated simultaneously through a T-piece, the arms of which are provided with stop-cocks and each connected with one of the flasks. The sample is sealed in a Victor Meyer bulb, wired on to the sealed end of the manometer tube projecting inside one of the flasks, the flasks evacuated to a pressure of about 1 cm. of mercury, and the cocks closed. The bulb may then be crushed by turning the arm attached to the T-piece, the end of which projects in the flask and is bent at an angle. If the temperature and increase in pressure are read after a few minutes the molecular weight (M) may be found from the equation $PV = WRT/M$. The minimum vapour pressure of the sample should be at least 4 cm. of mercury at room temperature, or larger flasks or a higher temperature must be used. J. G.

Spectrographic Chemical Analysis. H. Ramage. (*Nature*, 1929, 123, 601-602.)—The spectrographic analysis of minerals is conveniently carried out with a Hilger (C) quartz spectrograph on 0.5 gm. or less of sample tightly rolled in half an ashless (No. 00) filter paper, which is burnt for 25 minutes in an oxy-hydrogen or oxy-coal gas flame, a quartz lens being used to focus the flame on the slit. If the poles of an arc are placed horizontally in the flame just above the burning roll, the delicacy of the test is greatly increased, and elements such as titanium, molybdenum, tungsten, etc., give lines instead of only a continuous spectrum. Ilford panchromatic plates coated on thin glass are suitable for quantitative work, and the method has been applied to the examination of flue dust for gallium, to the determination of the salt content of different portions of plants grown in different soils or watered with different solutions, and to the determination of rubidium and other elements in blood or milk. Solid vegetable or animal substances may be held in forceps and burnt without the use of filter paper, while for liquids 0.1 c.c. is absorbed on the paper and burnt. J. G.

Barium Sulphate as Indicator of the Efficiency of Sulphuric Acid in Drying Apparatus. G. Boehm. (*Chem. Ztg.*, 1929, 53, 323.)—Sulphuric acid retains its desiccating properties until it is completely converted into the dihydrate (84.48 per cent. of H_2SO_4), which has the vapour pressure 0.131 mm. at 15°C ., whereas that of the trihydrate is 0.651 mm. Addition of about 18 grms. of barium sulphate to each litre of the concentrated acid allows the complete formation of the dihydrate to be detected. Until about one-half of the amount of water required to give the dihydrate has been absorbed, the acid shows no change. With further dilution, the compound $\text{BaSO}_4 \cdot 2\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ is increasingly precipitated in the form of acicular aggregates, which finally render the acid pasty. These crystals are not stable, and when the acid is wholly transformed into the dihydrate, are decomposed into finely crystalline barium sulphate. Thus, the acid need not be replaced so long as it contains acicular crystals. It is advisable to use the purest barium sulphate for this purpose, and the necessary quantity should be dissolved in a small portion of the sulphuric acid at 100°C . and afterwards mixed with the remainder of the acid. T. H. P.

Reviews.

STARCH: ITS CHEMISTRY, TECHNOLOGY AND USES. By LEWIS EYNON, B.Sc., F.I.C., and J. HENRY LANE, B.Sc., F.I.C. Pp. viii+256. Cambridge: W. Heffer & Sons, Ltd. 1928. 12s. 6d.

The authors state in their preface that it is now about forty-five years since a comprehensive text-book on starch has been published in the English language. In view of this fact, it is a curious coincidence that two books on this subject should

be published in the same year. Evidently when the authors' preface was written they were unaware of the book on starch chemistry, edited by Walton (see *ANALYST*, 1928, 53, 561), which was published some months earlier than their own. The ground covered is, for the most part, the same in both, but there are considerable differences in treatment, and each has one or two sections which the other has omitted.

In the book under review the authors, after giving a brief history of starch, deal in a very interesting and readable manner with starch in relation to plant metabolism. This is followed by a chapter on the constitution of starch. In this the authors discuss the various attempts which have been made to solve this problem since Kirchoff first discovered in 1811 that starch yields a sugar on hydrolysis with acid. The more recent work of Ling and Nanji, Irvine and others is discussed very clearly and in considerable detail. The following chapter deals with the properties of starch, and this will probably prove the most interesting portion to technical chemists. Much useful information regarding its gelatinising properties, and the viscosities of pastes and solutions of the more commonly used starches are given. In the section on the hydrolysis of starch the action of the various diastatic enzymes is discussed from the more purely biochemical aspect, *i.e.* no reference is made to the technical application of these reactions. The remainder of the chapter deals with its essentially chemical properties.

Chapter V, which is devoted to the microscopy of starch, describes very completely all the well-known starches, and many which are less well known to the British analyst. There are excellent reproductions of 32 photomicrographs of starches, but it is rather unfortunate that the magnification used is not indicated on the plates, and is only referred to in the last paragraph of the chapter. It would appear from the text that the authors intended the plates to follow at the end of the chapter, but the printers have inserted them a few pages in front. No doubt this small defect will be remedied in future editions.

Among the photomicrographs, it is interesting to note, the authors have inserted those of sago and tapioca in the ungelatinised form, as well as in the gelatinised. Generally only the latter are given, but now that the ungelatinised forms are so widely used in the foodstuff industries the former will prove more helpful to the analyst. Some special methods of identifying starches in mixtures are also given.

The next five chapters describe in considerable detail the technical preparation of starch from its various sources; then follows a chapter on the manufacture of such starch products as soluble starch, dextrin, dextrose, maltose, glucose syrups, etc., and numerous references are given to the various patents in connection with their manufacture. It should be noted that the authors confine themselves to starch and its immediate products, and do not deal with cereals or products in the manufacture of which starch or its products are used, beyond briefly outlining in Chapter X some of these industrial applications. In the latter section the authors describe under the term "confectionery purposes," such products as

custard powder, cake mixtures, etc., which, however, are not usually considered confectionery products. On the other hand, the only reference to the use of these substances in the confectionery and jam industries is contained in the previous chapter under the heading of starch sugar. Some reference might have been made to the very pure form of dextrose which the Americans have recently put on the market, and which will probably find use in the manufacture of entirely new types of confectionery, as well as in modifying some of the older forms.

The final chapter deals with the analysis of commercial starch and its immediate products. It does not, however, discuss methods for determining these in articles manufactured from them. A few examples of some of these would have added to the usefulness of the book to the general analyst.

The book, as one would expect from its authors, is very clearly written, and there is a remarkable absence of printers' errors. The printing and illustrations are good, and both Mr. Ward and the printers are to be congratulated on the excellence of the photomicrographs of the starches. It should prove a very useful book of reference to all who are interested in starch and its products.

T. MACARA.

PRACTICAL BACTERIOLOGY. AN INTRODUCTION TO BACTERIOLOGICAL TECHNIC.
By FRED W. TANNER, Ph.D., Professor of Bacteriology and Head of the
Department, University of Illinois. Pp. xiv+235, with 70 illustrations.
New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd.
1928. Price 12s. 6d. net.

The Society of American Bacteriologists has made some notable attempts to systematise the science of bacteriology. One activity has been the elaboration by a "Committee on Bacteriological Technic" of "Descriptive Charts." Professor Tanner was a member of the Committee that designed the latest of these charts in 1924. A copy of it is included in the book, and may be taken to exhibit current American opinion as to what morphological, cultural and physiological attributes require to be ascertained in the experimental investigation of an organism. Much of the book is devoted, either avowedly or in effect, to educating students to appreciate and to utilise the scheme for descriptive ends. A feature of this chart is the provision of many strange-sounding, but appropriate, adjectives to characterise the "form," "surface," "elevation," "edge," and "internal structure" of bacterial colonies, also the types of liquefaction in stab cultures, and the forms of growth in streak cultures. The selection of the right adjective, not always an easy decision, is assisted by a glossary and illustrations of colonies.

Another labour of the Society of American Bacteriologists, embodied but not, however, mentioned in the book, proves irksome to some English readers. This is the "Characterisation and Classification of Bacterial Types" which it evolved in 1920, together with its developments. Here the book gives no assistance. Nearly all other authors have recognised that the new classification is still

unfamiliar to many, and give the old as well as the American names. Here we have former nomenclature ignored. While we get accustomed to *Bacillus coli* changing its name to *Bacterium coli*, and then to *Escherichia coli*, while *Bacillus typhosus* goes to *Bacterium typhosum* and on to *Eberthella typhi*, such a name as *Aerobacter aerogenes* is not so easily recognised as identical with *Bacillus lactis aerogenes*, nor is *Serratia marcescens* indicative to many of *Bacillus prodigiosus*. That is, while admitting the American classification, we like to have the old names too.

The book is described as a "laboratory guide for students who are beginning the study of bacteriology," and the underlying idea is "to make students proficient in ordinary technic." It is calculated to do this with suitable students. There is nothing out of place in the book; even a digression on the attempts to explain and those to improve the Gram method of staining are valuable. Though little tangible result seems forthcoming, the recital directs attention to the degree to which chemical attributes, both of bacteria and of the materials used, do profoundly influence the success of the test. It is a striking comment that this dissertation should end with a quotation from C. J. Hucker and H. J. Conn, thus: "After a general survey of nineteen different methods of Gram staining, it is very difficult to select any one method as superior to all the others."

The author places the date of the discovery that some bacteria cells are Gram-positive when young, but Gram-negative when old, as late as 1921. Foulerton, in his classical lecture on Streptothricosis in 1910, gave instances of this obtaining in the Streptotricheae. Since then, but still before 1921, in 1916 the bacillus of malignant oedema, which had previously been characterised as Gram-negative, was found to be so when attenuated, but to be Gram-positive when young. Weinberg's *Bacillus oedematiens*, found in some gas-gangrene wounds during the war, was Gram-positive as a wound bacillus but Gram-negative in old cultures. Similarly, *Clostridium Chauvoei*, the causative organism of quarter-civil was known before 1921 as Gram-positive in the tissues and usually Gram-negative in culture.

Beef-extract broth is made to a composition unfamiliar in this country. [It is, however, printed in the formula for the basic broth used for the standard agar in the tests for graded milk (ANALYST, 1929, 235).] It omits addition of salt, and adds: "Earlier investigators added salt to this medium. It is not used to-day." The usual practice in this country has been and, I believe, largely is, to use five or ten grammes of salt to the litre. English formulae demand ten or twenty grammes of Lemco, but for very many years American workers have used three grammes of "beef extract" to the litre, sometimes specifying Lemco, sometimes not. Peptone is, similarly, reduced from twenty or ten grammes to five grammes per litre. However, Professor Tanner does not support the claims of such broth on the ancient plea, for which something can be said, that no later adjustment of reaction is usually necessary.

The use of white of egg for clarifying media is a very old device that meets with approval by most workers in this country and by some eminent Americans.

Professor Tanner says "this is not good practice, since it is known that egg contributes materials to the medium. Those who use egg in this manner prepare an egg agar, egg gelatin, etc. They do not secure a standard agar or gelatin medium." This seems to introduce the debateable points, firstly, whether a medium from which the coagulable part of egg has been removed by filtration can claim to be an egg medium, and, secondly, having regard to the invariably good results obtained with egg-clarified media for so many years, whether change of name would be preferable to change of practice.

The author avoids, as much as possible, the use of pathogenic bacteria in teaching, since "the continued study of pathogens tends to give a new student a warped idea of the science."

WILLIAM PARTRIDGE.

A COMPREHENSIVE TREATISE ON INORGANIC AND THEORETICAL CHEMISTRY.
Vol. IX. By J. W. MELLOR, D.Sc., F.R.S. Pp. 967. London: Longmans,
Green & Co. 1929. Price 63s. net.

The ninth volume of Mellor's compendious treatise deals with arsenic, antimony, bismuth, vanadium, columbium and tantalum. The treatise has now come to be regarded as an essential part of a chemical library, and chemists eagerly look forward with every confidence to the publication of the remaining volumes.

The new volume bears the characteristic traits of all Dr. Mellor's books, namely, systematic arrangement, exhaustiveness and completeness. Yet, despite his untiring and, indeed, superhuman energy in searching the vast chemical literature, apparently never missing a single important point, and then recording it all with astounding exactitude, we find that he has been able to find space, here and there, to give us many human touches. Thus the sections devoted to the historical and physiological aspects of arsenic and antimony compounds are particularly interesting, and might well be reserved for leisure reading.

Considered as a whole, the available and somewhat unwieldy matter has been assimilated and recorded in due perspective with regard to its importance. It must be confessed, however, that it is irritating to be continually confronted with almost barren phrases to the effect that X discussed this, and Y did that, without any indication as to their conclusions. This, perhaps, is inevitable in a comprehensive treatise of the size of Mellor's. Full references are included.

Dr. Mellor still hangs on tenaciously and slavishly to his nomenclature of inorganic substances, whether they be compounds or not. Fewer meaningless graphical formulae, however, are to be found in the present volume than in the earlier volumes.

The volume has been published in the usual satisfactory manner, and the proof-correcting seems to have been very thorough; only two misprints were seen, namely, "Rd." for "Radium," and an effect usually attributed to Thomson is coupled with the name of Thompson.

In conclusion, Dr. Mellor is to be heartily congratulated on the publication of yet another volume of his invaluable treatise, and must also be accorded the warmest appreciation and thanks of chemists on the great assistance he is continuing to render.

HUBERT T. S. BRITTON.

AMERICAN SOAP-MAKER'S GUIDE. AN UP-TO-DATE TREATISE ON THE ART AND SCIENCE OF THE MANUFACTURE OF SOAPS, CANDLES, AND ALLIED TOILET PREPARATIONS. By I. V. STANLEY STANISLAUS and P. B. MEERBOTT. Pp. 709. 105 Illustrations. London: Chapman & Hall, Ltd. 1929. 50s. net.

Described as "the most complete and exhaustive book in the English language," this book, while largely re-written and considerably expanded, is based partly on the second edition of Brann't's well-known "Soap-Makers' Handbook," published in 1912. It opens with a very interesting historical review of the soap industry from its earliest beginning to the present day, and then follows very much the usual conventional lines, the next eight chapters dealing with the constitution and properties of oils, and soaps, the more important fats and oils used, their preparation, bleaching and refining, and methods of examination. The simple triglycerides are still stated to form the preponderating constituents of oils and fats, and the conclusions of Hilditch in this country, and of Bömer and Ebach in Germany, that natural fats and oils consist mainly of mixed glycerides are ignored. The modern views as to the nature of soaps and soap solutions are well discussed, and the work of MacBain is given due recognition, but the erroneous statement in the previous edition that soaps are *soluble* in ether, benzol, and petroleum spirit, is here repeated. There is a very good and well illustrated description of modern methods of fat rendering, but the preparation of oils and fats by expression and extraction receives very scanty treatment. The section dealing with bleaching and refining has not been altered from the last edition, and was already out of date in 1912; even the mistake of calling bleaching powder *calcium chloride* has not been rectified. A chapter on Sulphonated and Hydrogenated Oils deals chiefly with the preparation, constitution, and analysis of sulphonated oils, hydrogenated oils being dismissed in about one page. Juillard's work on sulphonated oils is fully described, but nearly all the formulae he assigns to the products are wrongly quoted, and his name is misspelt Julliard (incidentally it occurs in the index as Juliard). Soap made from hydrogenated fish or whale oil is stated to have sometimes a slight fishy odour, this being less noticeable as the iodine value of the oil falls from 58° to 55° C. One chapter describes a number of suggested substitutes for fatty acids and soaps, emanating principally from Germany, and including several sulpho-derivatives; throughout this chapter the term carbohydrate is used where hydrocarbon is obviously intended. Thus tetralin, tetrahydronaphthalene, is quite wrongly referred to as a "partially hydrated carbohydrate."

For some unexplained reason there are two chapters on the analysis of oils, one headed Examination of Fats and Oils, the other General Tests for determining the Purity of Oils. Some processes, *e.g.* saponification value, and iodine value, are described in both, the former being dealt with at great length, and including four pages taken verbatim from a paper by A. H. Allen before this Society as long ago as 1886. The time recommended for saponification, *viz.* 10–20 minutes, would hardly be sufficient in the case of many oils, and 1 c.c. of $N/2$ KOH solution is wrongly stated to contain 280 mgrms. of potassium hydroxide. The only method given for determining the iodine value is that of Hübl, no reference being made to either the Wijs or the Hanus process. Many of the tests given are quite obsolete, such as testing for free fatty acids by pouring an oil on to cuprous oxide, and the determination of glycerin by oxidation with potassium permanganate in a strongly alkaline solution, which is said to be "the most reliable process." At the same time many important tests are not even mentioned, *e.g.* the refractive index, Halphen's test for cottonseed oil and Bellier's test for arachis oil, and the description of "solid foreign substances, such as fragments of skin, parts of plant, dirt, etc.," as unsaponifiable matter is quite incorrect according to the present day acceptance of this term.

There follow three chapters on the alkalis and their examination, water supply, lime for causticising alkali, and common salt. A well-illustrated chapter next describes soap pans, frames, crutchers, and other apparatus used in soap-making, and a good outline is then given of the various processes of soap manufacture, glycerin recovery and distillation being briefly dealt with under the process of soap-boiling. The seven following chapters describe, with formulae, the manufacture of the different qualities of household soap, both hard and soft, genuine and filled, textile soaps, washing powders, toilet soap (cold process, re-melted and milled), medicated soaps and shaving soaps. Some of the formulae appear rather unworkable, but these chapters give much useful information. One of the most important developments of recent times in the soap industry is the use of soap-coolers in place of frames, and it is surprising to find no reference to this subject, while other notable omissions are references to the manufacture of soap flakes and the use of per-salts in soap powders. The chapter on soap analysis has been brought more up to date, and gives methods for all the more important determinations. Some obsolete methods are still retained, and there is no reference to McNicol's method of determining rosin, which is now being officially adopted in this country. The only process for the determination of phenols is that found in most text-books, and attributed to Lewkowitsch, of salting out the soap from a strongly alkaline solution, filtering, concentrating the filtrate to small bulk, and acidifying in a graduated tube, in which the separated phenols may be read off. This method appears to have been quite generally abandoned in favour of precipitation of the phenols from their solution with a bromide and bromate solution standardised against a similar type of phenol. The determination of total fatty and rosin acids is detailed at length twice over, and it is out of place to find in this

chapter a test for unsaponifiable matter in an oil, twice repeated in almost identical terms, though first described as qualitative, and then as quantitative.

The essential oils and other materials used for perfuming soaps, and their method of compounding are dealt with in three following chapters, and here many of the mistakes of the last edition have been rectified. Some mis-statements, however, still appear, as with the specific gravity of bergamot oil, which is said to lie between 0.856 and 0.888, although the usually accepted limits are 0.880 to 0.886, and Bourbon geranium oil is quite erroneously stated to be obtained in the Presidency of Bombay from *Andropogon schoenanthus*, though in fact it is a true geranium or pelargonium oil emanating from the island of Réunion (Bourbon).

There is a short chapter on candle materials and manufacture, the latter being confined to a description of moulding only, and there are two more dealing with Toilet Creams and Dentifrices, these last consisting mainly of verbatim extracts, with the scantiest acknowledgment, from an English book on these subjects reviewed in this Journal a short time ago.

The book is well printed, and many of the illustrations are good, much better than in the last edition, but it has been compiled and passed for publication in an extraordinarily careless manner, possibly due to lack of proper collaboration between the two authors. In some cases whole paragraphs are repeated twice, and in many others they are inserted in the midst of quite irrelevant matter, whilst the number of misprints is astonishing. It can only be regarded both in its matter, and the manner of presentation, as a most disappointing book.

W. H. SIMMONS.

Publications Received.

THE PYROLYSIS OF CARBON COMPOUNDS. By C. D. HURD. New York: The Chemical Catalog Co., Inc. Price \$12.50.

THE CHEMISTS' YEAR BOOK, 1929. Edited by F. W. ATACK, R. T. ELWORTHY, and F. M. TURNER. Manchester: Sherratt & Hughes.

INDUSTRIAL CARBON. By C. L. MANTELL. London: Chapman & Hall. Price 21s. net.

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Furfural and Diastase in Heated Honey.

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THE presence of furfural and its derivatives in honey is generally stated in the literature to be indicative of the addition of commercial invert sugar to the natural product, but the claim is often made that a slight positive reaction (to the Fiehe test or to the furfuraldehyde test) may be obtained if the honey has been previously subjected to heat. Honey, in practice, is heated during the "vatting" process for mixing or blending, and it is therefore apparent that the whole question of the reaction of honey to the tests for furfural is of some importance.

The scheme of the work naturally falls under the following:—

- (a) Critical examination of the tests used hitherto for the detection of furfural and its derivatives in honey, with the development of the technique used in this work.
- (b) The literature referring to the interpretation of positive tests.
- (c) A study of the action of heat on honey with reference to the production of furfural.

To this has been added a short note on the effect of heat on the diastatic activity of honey, a point which also appeared of some interest.

TESTS FOR HYDROXY-METHYL FURFURAL AND FOR FURFURALDEHYDE IN HONEY.

HYDROXY-METHYL FURFURAL.—(a) *Fiehe's Test.*—The test, as originally described by Fiehe,¹ was as follows:—Ten grms. of honey are rubbed for 5 minutes

with sufficient ether in a mortar; the ether, which is coloured a pale yellow, is decanted off and evaporated to dryness at room temperature. To the residue so obtained are added 2 drops of 1 per cent. resorcinol in fuming hydrochloric acid. The production of an immediate cherry-red colour (sometimes violet tinted) is a positive indication of furfural derivative.

This method of procedure does not result in satisfactory extraction, and, moreover, the colour immediately formed is not a reliable indication because it changes rapidly.

(b) *Caillas's Modification*.—Caillas² criticises the method and suggests the following modification:—Extract 5 grms. of the honey in a test-tube with 5 c.c. of ether by shaking for one or two minutes, decant off the ethereal extract, to this add 2 c.c. of a freshly prepared 1 per cent. solution of resorcinol in pure hydrochloric acid, noting the immediate colour produced in the acid portion and the colour after standing for 20 minutes.

Here again the method of extraction is unsatisfactory.

(c) *A.O.A.C. (Tentative) Method*.—The A.O.A.C.³ specifies the following conditions:—Ten c.c. of a 50 per cent. solution of honey are extracted with 5 c.c. of ether; for the test a large drop of fresh 1 per cent. resorcinol in concentrated hydrochloric acid is added to 2 c.c. of the ethereal solution and shaken. It is directed that a cherry-red colour appearing immediately indicates commercial invert sugar, but that yellow or salmon shades have no significance.

Criticisms of this method are that only a small amount of honey is used and the size of the drop of reagent makes an appreciable difference in the results. We find that by this test it is not easy to detect 5 per cent. of commercial invert sugar added to a dark honey, though 10 per cent. can be detected fairly readily.

(d) *Roux and Muttelet's Modification*.—Further modifications described by Roux and Muttelet⁴ are as follows:—Twenty grms. of honey are dissolved in 20 c.c. of cold water, and the solution extracted with 20 c.c. of ether, which is then decanted and allowed to evaporate at room temperature, a few drops of resorcinol reagent being added to the residue.

The objection here is that, in the case of dark-coloured honey, the yellow residue, containing wax from the ethereal extract, changes the colour given by the reagent.

(e) *Method adopted for this work*.—We have found that most satisfactory results and most sensitive reactions can be obtained by employing a modified Roux and Muttelet method, using 40 c.c. of ether for the extraction and taking up the residue after the evaporation of the ether in a small quantity of the solvent, in order to minimise the effect of the coloured residue, but at the same time to retain the furfural material in a concentrated solution. The following are the details of the method we apply:—

Dissolve 20 grms. of honey in 20 c.c. of cold water and extract with 40 c.c. of ether, with gentle mixing; decant off the ether and evaporate at room temperature; dissolve the residue in 10 c.c. of ether, using 2 c.c. of this for the Fiehe test

and reserving the remainder for the aniline acetate test to be described later. To this 2 c.c. of ethereal extract add 2 c.c. of 1 per cent. solution of resorcinol in concentrated hydrochloric acid. A positive test is indicated by the immediate appearance of a pink colour in the acid layer; this rapidly darkens, until after 20 minutes there is a deep cherry-red colour at the junction of the acid and the ethereal layers.

It should be noted that the resorcinol reagent must be prepared freshly, as required, because the colour of the reagent changes to pinkish on keeping for even a short time, and darkens on further standing. It is also important that, in the test, the colour produced should be noted at the 20 minutes' interval; if the colour appears after that period, it should be disregarded. Only a definite cherry-red colour is of significance, brownish colours being disregarded.

FURFURALDEHYDE.—(a) *A.O.A.C. (Tentative) Method* (not applicable to dark coloured honey).—For this test the A.O.A.C.³ prescribes the following:—A reagent containing 100 c.c. of aniline and 30 c.c. of 25 per cent. hydrochloric acid (by weight) is used; 2.5 c.c. of this reagent are stirred directly into 5 grms. of honey. An orange to a dark red colour indicates the presence of commercial invert sugar, but yellow to salmon shades have no significance.

We have found it not easy by this method to detect 5 per cent. of added invert sugar, especially if the latter has a dark colour, although 10 per cent. gives a fairly definite result.

(b) *Leach Method (Browne's Test)*⁵.—The reagent is made by suspending 5 c.c. of aniline in 5 c.c. of water and adding glacial acetic acid to clear the emulsion (about 2 c.c. required). From 1 to 2 c.c. of this fresh reagent is poured carefully down the side of a test-tube containing 5 c.c. of a 50 per cent. solution of the honey, so as to form a layer on the surface of the honey solution. If, when the tube is gently agitated, a red ring forms beneath the aniline solution, this colour becoming gradually imparted to the whole layer, artificial invert sugar is present.

This method is preferable to the A.O.A.C. method, as the effect of the colour of the honey is not so great, but the colours obtained are not very definite.

(c) *Method used in this work.*—We prefer to carry out the test using the well-known aniline acetate reaction as commonly employed in testing for furfuraldehyde (the significance of which had already been studied by us),⁶ as follows:—

The ethereal solution put aside from the Fiehe test (*q.v.*) is evaporated at room temperature in a porcelain dish, and to the residue so obtained is added 2 c.c. of fresh aniline acetate solution made by dissolving 1 c.c. of redistilled aniline in 4 c.c. of glacial acetic acid. In positive tests a pink to orange colour appears within 15 minutes.

Both the Fiehe test and the aniline test as described will give distinct positive reactions with honey containing 5 per cent. of commercial invert sugar, strong colours in both cases being obtained when 10 per cent. of invert sugar is present.

Commercial invert sugar is considered to be present only when positive reactions are given by both the aniline acetate and Fiehe tests.

It is important that reagents (ether and acetic acid) should be free from furfural bodies, as ascertained by control tests.

LITERATURE REFERRING TO FURFURAL TESTS ON HEATED HONEY.—The following are the most important references to the interpretation of the results of furfural tests in connection with the effect of heat on honey:—

Leach⁴ states that boiled honey will give a positive aniline test for furfural, but adds that such treatment impairs the flavour and is probably never practised. In the Fiehe test an immediate orange to rose colour disappearing quickly may be due to heated honey.

Woodman⁷ considers that positive aniline chloride and Fiehe reactions are sometimes given by heated honey, but, usually in the case of honey heated to the temperature prevailing in commercial blending, the tests, if used with discrimination, will be found reliable.

Cox,⁸ referring to the application of Fiehe's test to heated honey, states that it may give a momentary pink colour if the heating has been sufficiently prolonged.

Muttele⁹ found that even after honey had been heated at 105–110° C. for three hours, yielding a caramelised product very much unlike honey in appearance and flavour, only very faint colours were produced in Fiehe's test.

Caillas¹⁰ claimed that the colour produced in the Fiehe test with honey containing 1 per cent. of added invert sugar could easily be distinguished from that given by heated honey. He found that heated honey gives no colour immediately, but on prolonged standing a cherry colour may be produced, though after 20 minutes the colour is very much lighter than would be obtained with 1 per cent. of invert sugar.

We have not been able to obtain such delicacy of reaction; probably this author used very light-coloured honey, and his invert sugar must have contained much furfural.

Voermans and Bakker¹¹ heated genuine honey for 6 hours in a boiling water-bath and also for 3 hours at 105° C., rendering the honey quite unpalatable, but the heated samples gave only transient and very slight rose colours in the Fiehe tests.

The A.O.A.C.¹² conducted some experiments on heated honey, but the results are not very consistent. The conclusion was that honey heated to 72° C. for 1 hour, 80° C. for $\frac{1}{2}$ hour, and 98° C. for 20 minutes gave negative Fiehe and aniline chloride tests, but the results may not be reliable, as three of the collaborators obtained negative results even on a honey containing 20 per cent. added invert sugar.

THE EFFECT OF HEAT ON HONEY.—The general procedure adopted by us in these tests was as follows:—

Samples of honey were placed in glass vessels, in thermostats at temperatures between 60° C. and 100° C. for periods from $\frac{1}{4}$ hour to 11 hours, with occasional stirring, small samples of about 30 grms. being withdrawn at intervals for examination.

The results of the application of the furfural tests to the various samples are shown in Table I (brown and white commercial honey) and Table II (English honey centrifuged from the comb). In all cases the unheated honey gave negative tests by both the aniline acetate and Fiehe tests.

TABLE I.

Temperature.	Time.	Aniline acetate test.	Fiehe test.
60° C.	Up to 1 hour.	—	—
65° C.	After 6 hours.	+	—
	After 8 hours.*	++	++
70° C.	After 5 hours.	++	—
	After 7 hours.*	++	+
80° C.	After 2 hours.	+	—
	After 4 hours.*	++	+
	After 5½ hours.*	++	++
90° C.	After 1 hour.	+	—
	After 2½ hours.*	++	++
100° C.	After ½ hour.*	+	+
	After 1 hour.*	++	++

* Indicates that the honey had become partly caramelised, the colour being decidedly darker than originally and the flavour also affected.

TABLE II.

Temperature.	Time.	Aniline acetate test.	Fiehe test.
60° C.	Up to 12 hours.	—	—
70° C.	After 6 hours.	+	—
	After 9 hours.	+	— (Very slight colour.)
	After 12 hours.	++	— (Very slight colour.)
80° C.	After 2 hours.	+	— (Very slight colour.)
	After 4 hours.*	+	+
	After 6 hours.*	++	++
90° C.	After 1 hour.	+	—
	After 2 hours.	+	++
	After 3 hours.*	++	++
100° C.	After ½ hour.*	+	—
	After 1 hour.*	++	++

* Indicates that the honey had become partly caramelised, the colour being decidedly darker than originally and the flavour also affected.

Reference to the tables will show that, in general, definitely positive results were only obtained in those cases where the colour and flavour had been affected and caramelisation had commenced. In other words, where the honey has been cooked sufficiently to give definitely positive furfural tests, it would be of little value from a commercial point of view on account of its flavour.

An explanation of the cause of the production of furfural in honey after prolonged heating may be found in the fact that the honey is slightly acid and that laevulose (but not dextrose) forms furfural compounds when treated with acids. The samples of honey used in these tests had an acidity equivalent to about 10–15 c.c. of *N*/10 caustic soda per 100 grms., corresponding to about 0.05 per cent. of formic acid. The P_H of 10 per cent. solutions ranged from 3.9 to 4.2. Proof of this explanation was obtained as follows:—

Samples of honey neutralised with caustic soda, and control samples of the same honey, were heated in a boiling water-bath for $1\frac{1}{2}$ hours. The control samples then gave strongly positive aniline acetate and Fiehe tests, but the neutralised samples gave no reaction (P_H of 10 per cent. solutions of control samples 4.0; of the neutralised honey 6.3).

The relative importance of laevulose and dextrose in this connection was also demonstrated. (In the following tests samples were first of all brought to a P_H of 4.0 for a 10 per cent. solution.)

- (a) Eighty grms. of laevulose + 20 c.c. of water heated to 100° C. for 15 minutes gave positive aniline acetate and Fiehe tests.
- (b) Seventy grms. of dextrose in 20 c.c. of water (this is a saturated solution) on heating at 100° C. for 1 hour gave negative aniline acetate and Fiehe tests, and on heating for a further hour, only a very slight pink colour was obtained in each test.
- (c) A 74 per cent. (saturated) solution of equal amounts of laevulose and dextrose gave positive results in both tests after heating for 15 minutes at 100° C.

INTERPRETATION OF POSITIVE FURFURAL TESTS.—As a result of our work we are of the opinion that if any sample of honey gives positive aniline acetate and Fiehe tests, it is adulterated with commercial invert sugar, unless there is marked evidence that strong heating has occurred.

It may be of interest to note that a sample of honey containing sufficient added commercial invert sugar to give positive furfural tests may still possess a ratio of laevulose: dextrose high enough for it to be considered genuine according to the results of Auerbach and Bodlander.¹³ These authors state that in genuine honey the ratio of laevulose: dextrose should not be less than 106: 100, and that for commercial invert sugar it is generally about 90: 100.

We would draw attention to the fact that there is on the market commercial invert sugar prepared by invertase in which the ratio is 99 or 100: 100 (this, of course, gives no furfural reaction).

We have determined this ratio on 310 samples of commercial honey of various origins and have obtained the following results:—

Fifty-two samples (17 per cent.) had a ratio of below 106: 100, 29 of them giving definite furfural tests; 94 samples (30 per cent.) had a ratio of from 106 to 110: 100, 8 of these giving positive furfural tests; 119 samples (38 per cent.)

had ratios between 110 and 120: 100, 5 of these giving positive furfural reactions; the remaining 46 samples (15 per cent.) had ratios between 120 and 169 to 100.

Samples of Californian honey extracted direct from the comb without heating had ratios of 107: 100, 115: 100, and 118: 100; two samples of English honey extracted direct from the comb had ratios of 114: 100 and 136: 100, respectively.

It is thus evident that the ratio of sugars in honey varies within wide limits, although it generally does not fall below 106: 100. It is therefore possible to add invert sugar to honey of high ratio and still obtain a product which has a ratio above the minimum limit; the above figures confirm this.

Auerbach and Bodlander¹³ further found that the ratio of laevulose to dextrose in honey increased with the time of storage, but determinations we have carried out have failed to reveal any such change.

THE EFFECT OF STORAGE ON HEATED HONEY.—In the J.A.O.A.C.¹³ it is stated that honey heated to 72° C. for 1 hour, 82° C. for 30 minutes, and 98° C. for 20 minutes gave negative furfural tests immediately after this treatment, but after keeping the treated samples at air temperature for 11 months, positive furfural tests were obtained in each case.

We have carried out similar tests, though so far samples have only been kept 8½ months, but they have not yet shown any development of furfural due to storing after heating. Details of some of the tests carried out in this connection are as follows:—

- (a) Two samples of honey heated at 50° C. for 6 hours gave, immediately after heating, a slight positive aniline acetate test, but negative Fiehe test, and similar results were obtained after 8½ months' storage.
- (b) Another honey gave negative tests by both methods after heating to 60° C. for 5 hours and to 70° C. for 4 hours, respectively, and also negative results in each case after the heated honey had been stored for 5 months.
- (c) Three other samples of honey which initially gave negative tests were heated as follows:—

Sample No. 1	.. 60° C. for 4 hours.	70° C. for 3 hours.
	80° C. for 1½ hours.	90° C. for ¾ hour.
Sample No. 2	.. 80° C. for 2 hours.	90° C. for 1 hour.
Sample No. 3	.. 60° C. for 4 hours.	70° C. for 4 hours.

All these samples gave negative tests immediately after heating, except in case 3, where slightly positive aniline acetate tests were obtained. After 6 months' storage in each case the results were still negative. Further tests will be made after longer periods of storing.

EFFECT OF HEAT ON THE DIASTATIC ACTIVITY OF HONEY.

LITERATURE REFERRING TO THE ENZYME ACTIVITY OF HONEY.—Several investigators have studied honey qualitatively from the standpoint of the enzymes present, but the determination of the activity of the enzymes in heated honey

has received little attention. Gothe¹⁴ reported the presence in honey of invertase, catalase, and diastase, and a few lesser known enzymes. He found that the invertase present had a maximum activity at 40° C., but was rendered inactive by heating the honey at 60° C. for one hour; that the catalase activity was strong in dirty honey, but that a low value did not necessarily mean a low grade or a heated honey; and that heating honey at 60° C. for one hour considerably reduced the catalase activity. From subsequent work on honey diastase¹⁵ he concluded that a high diastatic power indicates a pure honey, and that in the case of a honey of low diastatic power Fiehe's test must be applied before condemning the honey as adulterated. The diastatic activity was lost by heating above 70° C., but such treatment caused loss of aroma, and a honey so treated was considered a denatured product.

Invertase in honey was studied by Nelson and Cohn,¹⁶ who prepared an invertase solution from honey by alcohol precipitation followed by dialysis of an aqueous extract of the precipitate. The activity of this extract was determined on a sucrose solution.

DETERMINATION OF THE DIASTATIC ACTIVITY OF HONEY.—Two methods for the determination of the diastatic power of honey have been investigated by us, namely, Fiehe's modification of Gothe's method¹⁷ and Ohlsson's malt extract method.¹⁸

Auzinger¹⁹ studied diastase, catalase and peroxidase in various kinds of honey, but he carried out no quantitative work on heated honey. Qualitative tests showed that the diastase was destroyed at temperatures above 75° C.

The former method was used for several different samples of honey, and typical results obtained are given in Table III. Fiehe considered that honey

TABLE III.
GOTHE NUMBERS OF HONEY SAMPLES.

						Gothe number.
(1) Genuine honey	18.0
(2) Genuine honey	23.5
(3) Genuine honey	16.0
(4) Genuine honey	18.0
(5) Genuine honey	15.0
(6) Genuine honey	10.3
(7) Genuine honey	13.9
(8) Adulterated honey	13.0
(9) Containing 50 per cent. of added invert sugar						3.0

giving a number below 17.9 was to be regarded as suspicious, and below 10.9 as definitely adulterated. On this basis only samples 2 and 4 are satisfactory, yet only 8 and 9 gave positive furfural tests.

It appears, therefore, that Fiehe's standards require modification, but too much reliance cannot be placed on diastase tests, as heat considerably affects the diastatic power. This method was not further employed by us, as it did not prove suitable for the detection of small changes in diastatic power.

Ohlsson recognised the presence in malt extract of two enzymes: one he called "Saccharogen-amylase," which gives products in which reducing sugars (especially maltose) predominate, and the other "Dextrinogen-amylase," which gives predominantly dextrin when the malt extract is allowed to react with starch. The following method used by us for honey is a modification of that described by Ohlsson.

(a) *Dextrinogen-amylase*.—A series of tubes was prepared containing 1 c.c. of 0.2 per cent. starch solution, 8 c.c. of a phosphate buffer solution of P_H 5.6, and 1 c.c. of solutions of honey of various concentrations. The amounts of honey were arranged so that the quantity in one tube was 1.25 times that in the previous tube, convenient quantities being:—

10 per cent. solution, 1.0 c.c. 0.8 c.c. down to 0.26 c.c., made up to 1 c.c.

2 per cent. solution, — 0.85 c.c. down to 0.45 c.c., made up to 1 c.c.

(The P_H of the final mixture is about 5.7.)

The tubes were heated to 38° C. for 30 minutes for the diastatic action to take place, cooled in ice water, and 2 drops of $N/50$ iodine solution added. The colours of tubes then ranged from pale brown through purple to blue. The last pale brown and the first purple tubes, and the last purple and first blue tubes, were noted, the former colour boundary giving a value X for the diastatic power (for dextrin and reducing sugars), and the latter a value Y (for starch and dextrin).

The diastatic activity X or $Y = \frac{1}{2} (2/W + 2/W_1)$, where W and W_1 are the weights of honey in the two boundary tubes for each case.

Table IV gives the results on several samples of commercial honey.

TABLE IV.

	Dextrinogen-amylase.		Saccharogen-amylase.		
	X.	Y.	$\frac{1}{2}$ hour.	1 hour.	16 hours.
1. Californian honey direct from comb	30.8	39.2	1.0	1.5	33.9
2. English honey taken direct from comb	15.9	25.0	Nil	Nil	12.9
3. English honey	20.0	28.2	Nil	Nil	20.0
4. West Indian honey	36.4	48.8	3.15	7.2	36.3
5. West Indian honey	39.2	48.8	2.4	7.2	39.0
6. West Indian honey	39.2	54.7	2.6	6.6	30.9
7. Jamaica honey	44.0	60.6	—	—	—
8. Commercial blended honey, No. 1	39.2	48.8	4.7	5.2	28.4
9. Commercial blended honey, No. 2	25.0	35.2	1.6	2.5	27.3
10. Commercial blended honey, No. 3	40.0	54.7	2.6	2.6	30.7
11. Containing 50 per cent. invert sugar added	Nil	12.5	—	—	—

(b) *Saccharogen-amylase*.—Two 4 per cent. solutions of the honey were made, one with cold water, the other being boiled for about 15 minutes and serving as a control. Twenty-five c.c. of a 2 per cent. solution of soluble starch was placed in each of two flasks, 10 c.c. of a phosphate buffer (P_H 5.6) added to each and then warmed to 38° C. Ten c.c. of the honey solution were added to one flask, and the same quantity of the control honey solution added to the other flask, the mixtures heated at 38° C. for 30 minutes, also for 1 hour and for 16 hours. The flasks were cooled, the contents washed into 100 c.c. flasks, 10 c.c. alumina cream added, and the solutions made up to volume, filtered, and sugar determinations made by the Bertrand copper method, the results being expressed in equivalent of maltose. The diastatic power was taken as the number of mgrms. of maltose formed in the procedure as described above.

Ohlsson's method for malt extract specified 30 minutes' contact between the enzyme solution and the starch. With honey it was found that the amounts of maltose formed in that period were very small, and the reactions were therefore allowed to proceed overnight (16 hours). Table IV gives the values obtained with commercial honey.

It will be seen that where the honey has a high dextrinogen-amylase activity, the saccharogen-amylase activity is also high, and *vice versa*, and the orders of the activities are about the same in each case.

There is therefore definite evidence that honey diastase will act on starch, forming both dextrin and reducing sugars. The amounts of reducing sugars found for honey are very much lower than Ohlsson found for malt extract; in fact, they are of the order of those he obtained with pure dextrinogen-amylase solutions prepared from malt extracts, whence he concluded that dextrinogen-amylase can form small quantities of reducing sugars in addition to the dextrins. It is here suggested that a similar effect is obtained in honey and that saccharogen-amylase is not present, the sugars formed when honey reacts with starch being produced by the dextrinogen-amylase alone.

APPLICATION TO HEATED HONEY.—The method of heating was as described in the furfural section, in some cases both series of tests being carried out on the same sample of honey.

(a) *Dextrinogen-amylase*.—Some typical figures obtained on heated honey are given in Tables V and VI.

TABLE V.

Dextrinogen-amylase in Commercial Honey.

Temperature.	Time.	X.	Y.
<i>Sample I.</i>			
Original honey ..	—	44.0	68.8
90° C.	5 minutes	Nil	Nil
80° C.	10 minutes	25.0	35.2
	30 minutes	12.5	20.0

TABLE V.—*continued*.

Dextrinogen-amylase in Commercial Honey.			
Temperature.	Time.	X.	Y.
<i>Sample II.</i>			
Original honey	—	44.0	60.6
75° C.	2½ hours	8.0	12.5
	4 hours	Nil	5.1
70° C.	1 hour	31.3	44.0
	4 hours	15.9	25.0
	8 hours	6.4	11.5
	12 hours	Nil	Nil
65° C.	4 hours	31.3	45.0
	8 hours	25.0	31.3
	16 hours	12.5	20.0
	24 hours	10.6	12.5
60° C.	4 hours	39.2	48.8
	12 hours	31.3	44.0
	24 hours	25.0	31.3

TABLE VI.

On English honey direct from comb.

Temperature.	Time.	X.	Y.
Original honey ..	—	20.0	28.2
100° C.	5 minutes	Nil	Nil
80° C.	10 minutes	18.0	22.5
	1 hour	10.0	15.9
	2 hours	5.8	10.0
75° C.	1 hour	14.2	25.0
	4 hours	10.0	12.5
	8 hours	5.1	8.0
70° C.	1 hour	25.0	31.0
	6 hours	15.9	25.0
	12 hours	9.0	12.5
	18 hours	6.4	8.0
65° C.	4 hours	18.0	25.0
	12 hours	12.5	15.9
	24 hours	8.0	10.0
60° C.	4 hours	20.0	25.0
	12 hours	15.9	25.0
	24 hours	14.2	20.0

Table VII gives the time required for the destruction of half of the diastase as obtained from graphs plotted from the figures given in the preceding two tables.

These results show that the diastatic activity of honey (Dextrinogen-amylase) is considerably affected by heating, and at temperatures above 70° C. it is destroyed fairly readily.

TABLE VII.

Temperature.	Commercial honey.		English honey.	
	Halving period.	Complete destruction.	Halving period.	Complete destruction.
85° C.	Less than 10 minutes	15-20 minutes	20 minutes	1 hour
80° C.	12 minutes	80 minutes	1½ hours	3 hours
75° C.	Less than 2½ hours	4½ hours	3½ hours	More than 8 hours
70° C.	3 hours	12 hours	11 hours	More than 18 hours
65° C.	8 hours	More than 24 hours	15 hours	More than 24 hours
60° C.	20 hours	More than 24 hours	More than 24 hours	More than 24 hours

(b) *Saccharogen-amylase*.—Table VIII gives the saccharogen-amylase activity of the heated commercial honey used in the previous section.

TABLE VIII.

Temperature.	Time.	1 hour.	16 hours.
Original honey ..	—	2.6	37.9
70° C.	4 hours	0.5	13.6
	8 hours	0.5	9.0
	12 hours	0.4	3.4
	3 hours	2.0	28.2
65° C.	8 hours	1.5	20.6
	16 hours	0.4	11.7
	20 hours	0.5	8.1
	24 hours	Nil	7.1
	4 hours	2.0	36.7
	8 hours	1.0	27.1
60° C.	12 hours	1.0	25.9
	16 hours	0.5	22.3
	20 hours	0.5	21.8
	24 hours	Nil	21.2

The loss in saccharogen-amylase activity proceeds at approximately the same rate as the loss in dextrinogen-amylase activity noted previously. This is to be expected if the sugars formed by the action of honey diastase on starch are due to the dextrinogen-amylase alone, as was suggested above.

GENERAL SUMMARY.—(1) The methods described in the literature for the detection of furfural and hydroxy-methyl furfural in honey have been critically reviewed, and a technique developed for carrying out tests for these compounds in a satisfactory manner.

(2) It has been shown that heated honey may give positive reactions in these tests, but when this occurs the honey has been over-heated, so that the colour and flavour have been adversely affected.

(3) It is concluded that the presence of furfural and hydroxyl-methyl furfural in honey indicates that it has been adulterated with commercial invert sugar, or that it has been over-heated.

(4) Storage of heated honey has been shown to produce no development of furfural in a period of about 8 months.

(5) A technique has been evolved for the study of the diastatic activity of honey.

(6) Heating of honey causes a considerable loss in its diastatic activity, as would be expected, but the full significance of this has not yet been worked out.

The above work has been carried out in the Laboratories of Messrs. J. Lyons & Co., Ltd., to whom our thanks are due for permission to publish this paper.

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DISCUSSION.

The PRESIDENT remarked that very often papers were given which had a large title, but dealt with a small point. This was an example of the contrary; it was a paper with a small title, but dealing fully with a complicated matter, starting with a test which was widely used and but little understood, and then dealing with the factors influencing and underlying the test. He congratulated the authors on their valuable investigation.

Dr. H. E. Cox said that he would like to congratulate the authors on the thoroughness of their investigation; he envied the opportunity they had of examining so large a number of samples (320), which enabled them to draw conclusions with more certainty than most analysts who had a comparatively small number of such samples. He asked why there appeared a constant slight increase in diastatic activity in certain honeys on heating; also what was the approximate quantity of furfuraldehyde shown by the tests; how many parts per million did "a slight reaction" imply? Were there any pentoses or pentosans present which could give rise to furfural in small quantity? One reason why Fiehe's test was so

popular was perhaps that it was included in the German official regulations regarding artificial honey. Many data on the effect of heat on the enzymes of honey were contained in a paper by Auzinger (*Z. Unters. Nahr. Genussm.*, 1910, **19**, 65, 353), and they agreed, to some extent, with the authors' observations. Was there any evidence from the manufacturing side that honey was ever heated?

Mr. NORMAN EVERS mentioned the statement made by the authors that commercial invert sugar had been prepared with invertase. Had the Fiehe reaction been applied to this product? He stated that honey was sometimes heated for pharmaceutical purposes in order to get a darker colour, as some users of medicinal products liked this darker colour.

Mr. RENDLE asked if he might answer Dr. Cox's query: So far as he was aware, honey for edible purposes was heated only to facilitate blending, and therefore to as low a temperature and for as short a time as possible. With regard to the variation of diastase, had the authors determined any of the conditions which might influence this—for example, acidity?

The PRESIDENT here raised a point with regard to the diastatic power and asked whether, if one found a normal diastatic power, did this show that the honey had not been heated sufficiently to bring about the Fiehe reaction?

Mr. ROOKE, replying, said that with regard to the President's query about the normal diastatic power and the Fiehe reaction, sufficient work on this subject had, as yet, not been done by the authors of this paper, but they hoped to do it later. He would like to point out that where they had obtained definitely positive furfural reactions by the aniline acetate and Fiehe tests the honey was pretty well caramelised and not suitable for commercial use. Replying to Dr. Cox's query regarding the apparent increase of the diastatic activity, he said that they had not gone sufficiently into the question to answer this. He had no data on the subject of the quantity of furfural present in heated honey, but amounts of furfural and methylhydroxy-furfural were extremely small; for instance, the aniline acetate test would detect one part in ten millions of furfural. He mentioned a German (Troje) who worked out methods for the determination of methylhydroxy-furfural; his results were found to be erroneous by Fiehe himself, but were of the order of a few parts per million. With regard to the presence of any other substances, such as pentoses, in honey which might give furfural on heating, he pointed out that the acidity of honey was extremely small—0.05 per cent. as formic acid; he had also shown that the \bar{P}_H of 10 per cent. solutions of honey was 4, so that, even if pentoses were present, there was little likelihood of furfural being formed. Referring to the paper mentioned by Dr. Cox, he said that the literature on the subject was very contradictory and very difficult to follow up, because various authors had rather different criteria; for instance, Fiehe himself specified that the immediate colour must be noted; in the tests recorded in the present paper the authors had found that the immediate colours varied rather considerably and varied with the colour of the honey; thus, a dark-coloured honey might give a rather yellowish colour which might develop into a cherry-red, whereas a white honey might give an almost pure pink. With regard to the heating, honey was heated in some parts of the world before it was despatched to England in casks in what was known as the "vatting process," and heating might be as high as 70° C. Replying to Mr. Norman Evers's question regarding the presence of furfural in the invert sugar, he said that such invert sugar did not contain furfural, and with reference to the heating of honey for medicinal purposes, he had come across some very dark honeys which apparently were natural and,

he should imagine, quite suitable for the use mentioned. The authors had not yet gone into the effect of the acidity on the diastatic activity of the honey. He would like to make one other suggestion: apparently the diastase present in honey came from the flowers visited by the bees, and he thought it quite likely that flowers which grew in the tropics, for instance, might contain more diastase than those which grew in England.

Mr. HAIGH JOHNSON referred to the statement that the acidity was due to formic acid. He would like to know if this had been confirmed.

Mr. ROOKE replied that, personally, he had not made any tests on honey, but in the literature it was stated that the acidity was generally due to formic acid with, perhaps, some malic acid.

Some Analytical Applications of Sodium Hydrosulphite.*

(Antimony, Bismuth, Lead, Cadmium.)

By B. S. EVANS, M.C., Ph.D., F.I.C.

SODIUM hydrosulphite ($\text{Na}_2\text{S}_2\text{O}_4$), though extensively used by organic chemists, appears to have found very little application in inorganic analytical chemistry, and in particular one very curious group of reactions seems to have been overlooked altogether. In 1903 J. Meyer published a review of the chemistry of "hyposulphurous" acid (Meyer, *Z. anorg. Chem.*, 1903, **34**, 43-61), in which he made the statement that sodium hydrosulphite reduces salts of copper, silver, mercury, bismuth and selenium to the metallic state. The significance of this observation, from the analytical standpoint, lies in the fact that, unlike most other reductions to the state of metal, it takes place in alkaline solution, and therefore is not interfered with by many oxidising agents which would be fatal in an acid medium, notably nitric acid which is such a convenient solvent for most metals. An investigation of the reaction showed that not only the metals mentioned by Meyer, but others, notably lead, arsenic and antimony, could be precipitated; that potassium cyanide, whilst absolutely preventing the precipitation of copper, improves that of antimony (in fact it appears to be necessary for its quantitative separation); and that, at any rate for lead, antimony and bismuth, the separation is rapid and complete, the metal being obtained in the form of a dense black powder.

* Communication from the Research Department, Woolwich.

Many attempts were made to apply the reaction to the determination of arsenic, but so far without success, as it seemed impossible to precipitate the arsenic completely, at any rate in the presence of a large excess of, say, copper cyanide. The behaviour of the reagent towards cadmium was peculiar; it was not to be expected that metallic cadmium would be precipitated, and yet the early attempts made to separate cadmium from lead, antimony and bismuth always gave low results. This was eventually traced to the slow formation of cadmium sulphide which precipitated along with the reduced metals.

The ease and clean nature of the separations and the fact that, taking place in alkaline solution, they are not affected by the acid radicles present, and that consequently certain acids, *e.g.* nitric acid, do not have to be eliminated, suggested the application of the reaction to various determinations which are either difficult or very tedious. The following processes were worked out:—

(A) DETERMINATION OF ANTIMONY IN HIGH-ANTIMONY COPPER ALLOYS.

Certain acid-resisting commercial metals (*e.g.* "tant-copper") contain 4 or 5 per cent. of antimony alloyed with a large proportion of copper. In this case direct titration, such as might be carried out on a lead-antimony alloy, is entirely out of the question, and one is apt to fall back on a hydrogen sulphide separation, which is very cumbersome and tedious. The separation of antimony and copper by the alkaline sulphide method is not by any means complete in one precipitation, and it does not appear to be generally known that passage of hydrogen sulphide into an ammoniacal solution of antimony will actually cause precipitation of antimony sulphide which only very slowly re-dissolves as the liquid becomes saturated with the gas. The hydrosulphite separation of antimony from copper is clean, rapid and complete; details of the process are as follows:—

A weight of 1.0 grm., or a convenient amount, is dissolved in a mixture of 15 c.c. of hydrochloric acid, 5 c.c. of nitric acid, and 20 c.c. of water; 20 c.c. of a solution of 100 grms. of citric acid in 200 c.c. of water are added, and the liquid is made slightly alkaline with ammonia. A saturated solution of potassium cyanide is treated with bromine water until a drop removed gives no violet colour with a solution of sodium nitroprusside; the resulting solution is run into the ammoniacal solution of the sample until the blue colour is just discharged, and 20 c.c. in excess is added, followed by 50 c.c. of 20 per cent. ammonium chloride and 7 grms. of sodium hydrosulphite. The liquid is heated just to boiling point and allowed to stand on the steam-bath for 1 hour; about 2 grms. more of sodium hydrosulphite are then added, and the flask is placed in running water until completely cool.

The solution is next filtered through a pulp filter, and the precipitated antimony washed with a cold solution containing 20 c.c. of saturated potassium cyanide solution, 4 grms. of ammonium chloride, and 2 grms. of sodium hydrosulphite in 400 c.c.; filtration and washing should be carried out as quickly as possible to avoid any oxidation and re-solution of the finely divided antimony. It is desirable to heat the filtrate to boiling to make sure that no antimony has escaped precipitation; the solution should remain clear or contain only a cloud of

sulphur, and in this case it is rejected; should it, however, contain further antimony, the presence of this will be shown by the black precipitate; in these circumstances more hydrosulphite must be added, boiling continued for about a minute, and the liquid then allowed to stand, cooled, filtered and washed as before.

The filter or filters containing the antimony are transferred to a beaker and covered with a solution of bromine in dilute (1: 1) hydrochloric acid, the pulp is thoroughly broken up and stirred till all the antimony has dissolved, and the solution is then filtered off through a small pulp filter into a tall 800 c.c. beaker, and the pulp washed with dilute (1: 1) hydrochloric acid.

The antimony in the solution is determined by the method of Györy (*Z. anal. Chem.*, 1893, 32, 415), carried out as follows:—The bromine colour of the solution is discharged with sulphurous acid, and 25 c.c. excess added; the liquid is then boiled down to about 10 c.c. with a cover on the beaker; it is diluted with a mixture of 10 c.c. of hydrochloric acid and 120 c.c. of water, which is used to rinse down the cover glass and sides of the beaker; it is again heated to boiling, 3 drops of methyl orange solution (0.1 per cent.) are added, and it is cautiously, drop by drop, titrated with standard potassium bromate solution until the colour is just discharged, the temperature not being allowed to fall below 80° C. If the amount of antimony is approximately known it is preferable to add the bromate solution to within about 3 c.c. of the required amount before adding the methyl orange; it is then again heated to boiling, and the titration cautiously finished, drop by drop.

The following results were obtained in a series of trials on electrolytic copper to which varying amounts of antimony had been added:—

Copper taken. Grm.	Antimony added. Grm.	Titration.		Antimony.	
		Theoretical.	Actual.	Added. Per Cent.	Found. Per Cent.
1.0	0.0898	29.35	29.25	8.16	8.14
1.0	0.0719	23.50	23.30	6.72	6.66
1.0	0.0539	17.60	17.65	5.13	5.14
1.0	0.0360	11.75	11.65	3.46	3.43
1.0	0.0180	5.90	5.90	1.76	1.76
1.0	0.0090	2.95	3.00	0.89	0.91

(B) DETERMINATION OF SMALL AMOUNTS OF BISMUTH IN TIN-ZINC ALLOYS.

The difficulty of this determination lies in the fact that, tin and zinc both being present, it is not possible to carry out an ordinary hydrogen sulphide separation without getting a bulky and unwashable precipitate of either tin or zinc sulphide, unless the acid content is so high as to interfere with the precipitation of the bismuth. On the other hand, precipitation of the bismuth as hydroxide also precipitates the tin, whilst precipitation of the tin as metastannic acid drags down the bismuth almost quantitatively. The following method proved to be rapid and accurate:—

A 5.0 grm. portion of the alloy is dissolved in 30 c.c. of hydrochloric acid, diluted with 20 c.c. of water, 5 c.c. of nitric acid being added after the first violent

action is over; 15 grms. of tartaric acid and about 5 c.c. *N*/10 arsenious oxide* are added, and the solution is made alkaline with ammonia. Five grms. of ammonium chloride are added, followed by 40 c.c. of saturated potassium cyanide solution which has been treated with bromine water in the manner described in the preceding method, and, finally, 7 grms. of sodium hydrosulphite.

The resulting solution is heated to boiling, allowed to stand on the steam-bath for 1 hour, about 2 grms. of sodium hydrosulphite are added, and the flask is cooled in running water until quite cold. The mixed bismuth and arsenic precipitate is filtered off through a pulp filter and washed with the solution described for washing the antimony precipitate in the preceding method; the filtrate and washings are discarded. Re-heating of the filtrate will always show a precipitate, but this is arsenic, and not bismuth, which is completely precipitated.

The filter is transferred to a beaker and covered with a solution of bromine in dilute (1:1) hydrochloric acid, the pulp is thoroughly broken up with a glass rod and stirred until the precipitate is completely dissolved, after which the liquid is filtered through a small pulp filter into a beaker, and the pulp is washed 2 or 3 times with dilute (1:1) hydrochloric acid and 2 or 3 times with water. The filtrate is boiled down, 20 c.c. of dilute (1:3) sulphuric acid are added, and it is heated till all hydrochloric acid is driven off, after which a few drops of nitric acid are added to destroy the brown colour due to the charring of fibres from the filter, and it is again heated until the sulphuric acid fumes strongly. The beaker is allowed to cool, the acid liquid is diluted with 15 c.c. of water, boiled, cooled and rinsed into a Nessler glass and the bismuth determined colorimetrically by the bismuth iodide process.

To carry out this process, 10 c.c. of a saturated solution of sulphur dioxide diluted ten times are added, followed by 10 c.c. of 4 per cent. potassium iodide solution, and the liquid is made up to the mark with water; in the standard glass are placed 20 c.c. of dilute (1:3) sulphuric acid and 10 c.c. each of the two reagents; standard bismuth sulphate solution (1 c.c. = 0.0001 gm. Bi.) is run into the standard glass until the colours match.

Tests of the process were made on mixtures of tin and zinc to which varying amounts of bismuth had been added. The following results were obtained:—

Tin taken. Grms.	Zinc taken. Grms.	Bismuth added. Grm.	No. of c.c. reqd.		Bismuth recovered. Grm.
			Total.	Net.	
3.0	2.0	Blank on Sn and Zn	2.0	—	—
3.0	2.0	0.0001	3.0	1.0	0.0001
3.0	2.0	0.0002	4.0	2.0	0.0002
3.0	2.0	0.0003	5.0	3.0	0.0003

(C) DETERMINATION OF SMALL AMOUNTS (0.01–0.20 PER CENT.) OF ANTIMONY IN LEAD AND LEAD ALLOYS.

High amounts of antimony alloyed with lead are easily determined by direct solution of a small sample in a solution of bromine in hydrochloric acid and

* Arsenic is added in the process to produce a filterable precipitate, as the amount of bismuth is so very small.

determination by Györy's volumetric potassium bromate method. Minute amounts (up to, say, 0.05 per cent.) may be determined by the method published by the author (ANALYST, 1927, 52, 565), or, better, by this method finished by S. G. Clarke's colorimetric determination (ANALYST, 1928, 53, 373). Between these two ranges, however, is a short gap which does not lend itself readily to either method of determination; on the one hand, the quantity (say 0.1 per cent.) is rather too large for accurate colour work; on the other, the bromate titration is not very accurate for small amounts (say under 0.007 grm., representing 0.14 per cent. on a 5 grm. sample), and one is precluded from using a larger sample to get a higher titration value by the impossibility of getting it to dissolve directly in bromine and hydrochloric acid. The method described by the author (ANALYST, 1927, 52, 568), whilst working perfectly for the determination of tin, is inadmissible in the case of antimony, owing to the fact that antimony would undoubtedly be extracted from the red rubber stoppers, connections, etc. The following process was devised to cover the above-mentioned gap:—

A sample weight of 20 grms. (which need not be finely divided) is dissolved in 100 c.c. of dilute nitric acid (sp. gr. 1.2) to which 5 grms. of tartaric acid have been added. The crystallised lead nitrate is dissolved by the addition of hot water, the solution is heated to boiling, 80 c.c. of dilute (1:3) sulphuric acid is added, and the liquid is cooled, filtered, and the precipitate washed with 2 per cent. sulphuric acid. The filtrate is made slightly alkaline with ammonia, 20 c.c. of a saturated solution of potassium cyanide which has been treated with bromine water, as described in the process for determining antimony in copper-antimony alloys, is added, followed by 7 grms. of sodium hydrosulphite, and the whole is heated to boiling, allowed to stand for 1 hour on the steam-bath, and finished as described in the process for determination of antimony in copper antimony alloys.

The following results were obtained with a sample of lead to which varying amounts of antimony had been added; some results are also shown for a sample of lead to which 2 per cent. of tin, in addition to the antimony, had been added:—

Lead taken. Grms.	Tin taken. Grm.	Antimony added. Grm.	No. of c.c. KBrO ₃ soln.			Antimony.	
			Total.	Net.	Calc.	Added. Per Cent.	Recovered. Per Cent.
20.0	—	Blank on lead	0.70	—	—	—	—
20.0	—	0.0045	2.10	1.40	1.45	0.022	0.021
20.0	—	0.0090	3.40	2.70	2.90	0.045	0.041
20.0	—	0.0179	6.20	5.50	5.80	0.089	0.084
20.0	—	0.0268	9.10	8.40	8.70	0.134	0.129
20.0	0.40	Blank on lead and tin*	0.25	—	—	—	—
20.0	0.40	0.0092	3.15	2.90	3.00	0.046	0.044
20.0	0.40	0.0184	6.20	5.95	6.00	0.092	0.091

* A different sample of lead.

Subsequent to obtaining the above figures it was found that, contrary to expectations, cadmium exercised a retarding effect on the precipitation of antimony, being itself precipitated as sulphide; in the presence of cadmium, therefore, a slight modification of the process is required. The method is followed exactly up to the point where the potassium cyanide has been added, the solution is then heated to boiling, 7 grms. of sodium hydrosulphite are cautiously dropped in, boiling is continued for ten minutes, followed by a ten minutes' stand on the steam-bath; from this point on, the original process is followed. The method was tested on 5 gm. samples of lead, to each of which 0.04545 gm. of antimony and varying amounts of cadmium had been added, with the following results:—

Lead taken. Grms.	Antimony added. Grm.	Cadmium added. Grm.	Titration.		Antimony.	
			Actual c.c.	Calculated c.c.	Added. Per Cent.	Found. Per Cent.
5.0	0.04545	0.010	15.15	15.15	0.909	0.909
5.0	0.04545	0.020	15.20	15.15	0.909	0.912
5.0	0.04545	0.030	15.15	15.15	0.909	0.909
5.0	0.04545	0.040	15.10	15.15	0.909	0.906

(D) SEPARATION OF CADMIUM FROM BISMUTH AND LEAD.

It seemed likely that hydrosulphite precipitation would prove a ready method of separating cadmium from bismuth, antimony, and the traces of lead that are so much trouble to eliminate in the determination of cadmium in lead and lead-base alloys. As stated above, the separation of antimony from cadmium by the methods given so far is quite out of the question; in the case of lead and bismuth, trials showed that approximate, but low, results were obtained.

Quantities of 5 grms. of lead, 0.05 gm. of bismuth, and 0.1 gm. of antimony were taken, and varying amounts of cadmium were added. The samples were dissolved in nitric acid (sp. gr. 1.2), the bulk of the lead thrown out as sulphate, citric acid added, the antimony removed by the sodium sulphide method and the precipitated sulphides of lead, bismuth and cadmium, after washing with 5 per cent. potassium nitrate solution, dissolved in hot dilute *aqua regia*. The solution was made alkaline with ammonia, 1 or 2 grms. of potassium cyanide (A.R) and 2 grms. of sodium hydrosulphite added, and the liquid heated to boiling, allowed to stand for 10 minutes on the steam-bath, cooled, filtered, and the precipitate washed with the solution described for washing the antimony precipitate in method (A) of this paper. Hydrogen sulphide was passed into the filtrate, and it was allowed to stand on the steam-bath for $\frac{1}{2}$ hour (a clear yellow precipitate was obtained in three out of the four determinations); it was then filtered, washed with 2 per cent. ammonium nitrate solution, dissolved in hot dilute *aqua regia*, evaporated with addition of 5 c.c. of dilute (1:3) sulphuric acid until it fumes, transferred to a weighed platinum dish, evaporated, ignited at a temperature of

about 500° C., and weighed. These experiments gave the following results:—

	Lead taken. Grms.	Bismuth taken. Grm.	Antimony taken. Grm.	Cadmium added. Grm.	Cadmium found. Grm.	Weight of CdSO ₄ obtained. Grm.
(a)	5.0	0.05	0.10	0.0100	0.0082	0.0168
(b)	5.0	0.05	0.10	0.0200	0.0181	0.0352
(c)	5.0	0.05	0.10	0.0300	0.0308	0.0588
(d)	5.0	0.05	0.10	0.0400	0.0370	0.0702

Experiment (c) was the one which gave a dark-coloured sulphide, which explains the higher result. This may have been due to incomplete separation of the antimony in the preliminary treatment, as the antimony determined on the sulphide filtrate gave a lower result than in the other experiments. It was noted, however, in trials made on cadmium alone that no precipitation of cadmium sulphide took place until the solution was actually, or at any rate nearly, boiling; on the other hand, lead and bismuth both precipitate at temperatures far below boiling point, and the two precipitates being totally unlike in character, on the one hand a direct precipitation of colloidal sulphide (owing, presumably, to the formation of sulphide in the solution), on the other, a reduction to, probably crystalline, metal, there seemed little likelihood of an adsorptive dragging-down of the cadmium, such as would almost certainly have taken place if the two reactions had been similar.

It seemed worth while, therefore, to try and effect a separation at, say, 60° C. Quantities of 0.05 gm. of lead,* 0.05 gm. of bismuth, and varying amounts of cadmium were brought into solution with nitric acid, 10 c.c. of citric acid solution (100 grms. of citric acid to 200 c.c. water) were added, and the solutions made alkaline with ammonia; about 1 gm. of potassium cyanide (free from sulphide) was added to each, followed by 7 grms. of sodium hydrosulphite. A thermometer was placed in the solution, which was heated on the steam-bath to a temperature of 60° C.; the flask was then removed and allowed to stand on the bench for $\frac{1}{4}$ to $\frac{1}{2}$ hour; it was then filtered through pulp, and the precipitate washed with the washing liquid described above. Hydrogen sulphide was passed through the filtrate, which was then heated to boiling and allowed to stand on the steam-bath until the cadmium sulphide had separated sufficiently to allow of filtration; it was then filtered. The precipitate was thoroughly washed with 2 per cent. ammonium nitrate solution and burnt off in a weighed porcelain crucible at a low heat.

After cooling, the residue in the crucible was treated with 9 drops of dilute (1:3) sulphuric acid and 2 drops of concentrated nitric acid, the liquid was evaporated off, and the crucible very gently ignited at a temperature of about 500° C. and weighed; a blank determination was made by washing a pulp filter with 2 per cent. ammonium nitrate solution, burning off in a weighed platinum dish, treating with 9 drops of dilute (1:3) sulphuric and 2 drops of nitric acid, and finishing as described for the experiment; the weight of this blank was deducted

* This quantity was taken as being considerably more than the amount left in solution after an ordinary sulphuric acid precipitation of lead.

from the weight of crude cadmium sulphate found, and the remainder calculated to cadmium. The following results were obtained:—

Lead taken. Grm.	Bismuth taken. Grm.	Cadmium added. Grm.	Cadmium found. Grm.	Corrected weight of cadmium sulphate. Grm.
0.05	0.05	0.0100	0.0101	0.0188
0.05	0.05	0.0100	0.0101	0.0188
0.05	0.05	0.0200	0.0197	0.0366
0.05	0.05	0.0300	0.0301	0.0558
0.05	0.05	0.0400	0.0399	0.0740

To prove that the substance obtained was really cadmium sulphate, and not merely a low amount of cadmium sulphate balanced by some adsorbed alkali salt, the residues in the crucibles were dissolved in dilute (100 c.c. of water : 7 c.c. of 1:3 sulphuric acid) sulphuric acid, and the solutions saturated with hydrogen sulphide; after standing overnight the cadmium sulphide (which again was pure yellow) was dissolved in hot dilute *aqua regia* and finished as described by A. T. Etheridge (ANALYST, 1924, 49, 575). The results obtained were as follows:—

Weight of cadmium taken. Grm.	Original weight of of cadmium found. Grm.	Weight of cadmium found after acid H ₂ S precipitation. Grm.
0.0100	0.0101	0.0099
0.0200	0.0197	0.0195
0.0300	0.0301	0.0299
0.0400	0.0399	0.0393*

* In this experiment a minute fragment of cadmium sulphide was lost.

These experiments show conclusively that the loss of weight after acid hydrogen sulphide is within the limits of experimental error; also, that an alkaline sulphide precipitate treated in the way described gives substantially correct results, and that lead and bismuth can be separated completely from cadmium by means of sodium hydrosulphite.

SEPARATION FROM ANTIMONY.—There still remained the problem of separation from antimony, which forms a constituent of a large proportion of the lead cadmium alloys. The sodium sulphide separation, by adding another operation to be performed, increases considerably the length of time taken in the determination of the cadmium. As stated above, it is impossible to separate antimony and cadmium by boiling with hydrosulphite, and a pure antimony solution does not begin to precipitate until just below the boiling point. It will be observed, however, that we are here dealing with a mixture which is the converse of the bismuth and cadmium mixture referred to above; in that case the cadmium sulphide precipitate was of a radically different character from the metallic precipitate of bismuth, and therefore the cadmium did not show any tendency to co-precipitate with the latter at 60°; in this case, antimony, lead and bismuth all form metallic precipitates, only distinguished by the temperatures at which they come down,

and one would expect considerable co-precipitation of antimony with either lead or bismuth at 60°.

It seemed worth while to attempt a separation on these lines. Solutions containing 0.05 grm. of lead, 0.10 grm. antimony, and varying amounts of cadmium were taken; 0.2 grm. bismuth in the form of a solution of the nitrate was added to each (this with a view to providing sufficient precipitate to drag down the antimony) followed by 10 c.c. of citric acid solution (50 grms. of citric acid : 100 c.c. water); the solutions were made alkaline with ammonia and 20 c.c. of dilute (1:1) ammonia added in excess, 10 c.c. of saturated solution of potassium cyanide treated with bromine water, as already described, were added, and, finally, 7 grms. of sodium hydrosulphite. A thermometer was placed in the liquid and it was heated to 60° C. on the steam-bath, then allowed to stand for 15 minutes, filtered through pulp and washed as described above. Hydrogen sulphide was passed through the filtrate for several minutes, and it was heated to boiling, allowed to stand for 1 hour on the steam-bath, filtered through pulp, and the precipitate washed with 2 per cent. ammonium nitrate solution. The precipitate, which in every case was of a clear golden yellow, was burnt off in a weighed porcelain crucible and finished as described under the separation of cadmium from lead and bismuth.

The following results were obtained:—

Lead taken. Grm.	Antimony taken. Grm.	Bismuth taken. Grm.	Cadmium added. Grm.	Cadmium found. Grm.	Cadmium sulphate obtained. Grm.
0.05	0.10	0.20	0.0100	0.0102	0.0190
0.05	0.10	0.20	0.0200	0.0196	0.0360
0.05	0.10	0.20	0.0300	0.0300	0.0556
0.05	0.10	0.20	0.0400	0.0395	0.0732

The above figures show that by this process cadmium can be determined in the presence of antimony, as well as of lead and bismuth. For all that, however, it must not be supposed that co-precipitation with lead or bismuth by hydrosulphite removes all antimony from solution; on the contrary, a large number of experiments have shown that a small, but appreciable, amount of antimony remains in the solution; what the hydrosulphite has done, in addition to completely removing lead and bismuth, is to bring down the antimony concentration so far that it does not precipitate in the ammonium sulphide liquid in which the cadmium is precipitated. If, however, after the cadmium has been thrown down the liquid is boiled (or even allowed to stand, hot, for any length of time), the remaining antimony precipitates as sulphide, as is shown by the darkening of the precipitate. Addition of ammonium sulphide restores the yellow colour to the precipitate, and it is a wise precaution to add it, whatever the colour, subsequent to heating to the boiling point and to allow the flask to stand on the bench and not on the steam-bath for the cadmium sulphide to settle out.

In applying the process finally to the determination of cadmium in lead base alloys an unexpected difficulty was encountered; losses persistently occurred which

were at last traced back to the sulphates derived from the sulphuric acid used in precipitating the lead. Apparently some difficultly soluble compound of cadmium is formed which is filtered off with the precipitated metals. It was found, however, quite easy, and, in fact, considerably simpler and quicker to throw down the whole of the lead with hydrosulphite, thus avoiding the use of sulphuric acid at all. The quantity of hydrosulphite required for 5 grms. of lead is only 10 grms., and the lead is completely and cleanly removed along with the bismuth and most of the antimony in one operation taking, perhaps, 20 minutes.

PROCESS OF DETERMINATION.—The complete process worked out for the determination of cadmium in lead antimony (bismuth if present) alloys is as follows:—

A sample weight of 5 grms. of the alloy is dissolved in 50 c.c. of citric acid solution (50 grms. of citric acid : 100 c.c. of water) and 50 c.c. of dilute nitric acid (sp. gr. 1.2); the solution is neutralised with ammonia, and 20 c.c. of dilute (1:1) ammonia added in excess, followed by 10 c.c. of saturated potassium cyanide which has been treated with a few drops of bromine water. The solution is cooled, 10 grms. of sodium hydrosulphite dropped in, and the liquid gently swirled, care being taken not to let the liquid mount high up the walls of the flask, because the white precipitate first formed adheres to the glass, and, though reduced and detached when the solution gets hot, is inaccessible in the upper parts of the flask. A thermometer is inserted in the liquid, which is then heated to 60° C. on the steam-bath, being shaken gently when the precipitate begins to blacken and fairly vigorously as the temperature gets higher. When the temperature reaches 60° the flask is removed from the bath, cooled, the liquid filtered through pulp, and the precipitate washed* with the solution described earlier for washing the antimony in section (A) of this paper.

To the filtrate are added 10 c.c. of ammonium sulphide solution (made by saturating dilute (1:1) ammonia with hydrogen sulphide) the liquid is heated just to boiling, removed from the plate, 10 c.c. more of ammonium sulphide solution are added, and the flask is allowed to stand on the bench for half an hour. As an alternative to the use of ammonium sulphide, hydrogen sulphide can be passed through the filtrate in a rapid stream for 10 minutes for the initial precipitation, and, after heating, 20 c.c. of dilute (1:1) ammonia are added, and a current of hydrogen sulphide again introduced.

The precipitate, which should be of a pure golden yellow colour, is filtered off through pulp, well washed with 2 per cent. ammonium nitrate solution, burnt off at a low temperature in a weighed porcelain crucible, cooled, treated with 9 drops dilute of (1:3) sulphuric acid and 2 drops of nitric acid, evaporated to dryness, gently ignited at a temperature just below red heat, cooled, and weighed. A small blank, due to the filter ash and any residue in the sulphuric and nitric acids, must be deducted from the weight of cadmium sulphate. The entire process, from start to finish, takes about five hours.

* This is best done by decantation.

The following results were obtained with samples which had already been analysed by the ordinary process:—

Lead (by diff.) Per Cent.	Antimony. Per Cent.	Copper. Per Cent.	Cadmium by old process. Per Cent.	Cadmium by hydro- sulphite process. Per Cent.
97.42	1.77	—	0.81	{ 0.82 0.82
97.99	0.50	—	1.51	1.50
98.22	0.47	—	1.31	1.32
99.16	0.50	0.11	0.23	0.22
97.04	2.00	—	0.96	0.94

If tin is present, it must be removed before the hydrosulphite treatment; this is due to the fact that tin prevents the precipitation of cadmium by ammonium sulphide. This curious reaction, which appears to have escaped notice, is being investigated further. The tin is easily removed as metastannic acid, which does not appear to adsorb cadmium; the sample is dissolved in nitric acid without the addition of citric acid, the solution is evaporated to dryness, the residue taken up with dilute nitric acid, filtered, and the residue washed with dilute nitric acid. To the filtrate are added 50 c.c. of the citric acid solution, and the liquid is made alkaline with ammonia, potassium cyanide and sodium hydrosulphite added, and the remainder of the process carried through as already described.

It would seem probable that almost all the other commoner metals could be separated from cadmium by this process. Needless to say, zinc would not be separated and would require the usual acid sulphide separation. Large amounts of sulphates must not be present.

The Volumetric Determination of Mercury.

BY H. B. DUNNICLIFF, M.A., Sc.D., F.I.C., AND H. D. SURI, M.Sc.

(Read at the Meeting, December, 1928.)

NUMEROUS methods have been proposed for the volumetric determination of mercury.

F. M. Litterscheid (*Arch. Pharm.*, 1903, 241, 306) precipitated mercury from mercuric chloride solution by a standard solution of potassium dichromate and ammonia and determined the excess of dichromate in the filtrate by an iodimetric method.

L. W. Andrews (*Amer. Chem. J.*, 1903, 30, 187) analysed mercuric chloride by adding excess of a neutral solution of hydrocyanic acid and titrating the liberated hydrochloric acid against a standard alkali.

E. Rupp (i) (*Arch. Pharm.*, 1903, **241**, 328) determined the mercury in mercuric cyanide by an iodimetric method; and (ii) (*ibid.*, 1905, **243**, 300) reduced a mercury salt to metallic mercury with alkaline formaldehyde. The mercury was dissolved in excess of *N*/10 iodine solution, and the excess of the iodine was determined by thiosulphate.

E. Ebler (*Z. anorg. Chem.*, 1905, **47**, 377) reduced the mercuric salt with excess of *N*/40 hydrazine sulphate, and determined the excess of hydrazine with standard iodine.

P. W. Robertson (*Chem. News*, 1907, **95**, 253) precipitated mercury as $\text{ZnHg}(\text{CNS})_4$ by standard ammonium thiocyanate and excess of zinc sulphate, and determined the excess of thiocyanate in the filtrate.

H. Morawitz (*Z. anorg. Chem.*, 1908, **60**, 456) titrated mercuric chloride against *N*/10 potassium cyanide, with *p*-nitrophenol as indicator.

J. Knox (*J. Chem. Soc.*, 1909, T., **95**, 1768) found that the results obtained by Rupp and Kraus's method for the determination of mercury by titrating against ammonium thiocyanate (*Ber.*, 1902, **35**, 2015) were low. This he ascribed to contamination of mercuric nitrate by mercurous nitrate.

E. Rupp and F. Lehmann (*Chem. Ztg.*, 1910, **34**, 229) determined mercury in the presence of silver by treating a suitable quantity of the nitric acid solution with an alkaline solution of potassium iodide, making up to a definite volume and filtering. The mercury in the filtrate was determined by E. Rupp's formaldehyde method (*loc. cit.*, ii).

F. Reinthaler (*Chem. Ztg.*, 1911, **35**, 593) reduced mercuric chloride or nitrate with excess of standard *N*/10 arsenious acid. The excess of arsenious acid was then determined iodimetrically.

G. S. Jamieson (*Amer. J. Sci.*, 1912, [iv], **33**, 349) determined calomel by means of standard potassium iodate.

J. E. Clennell (*Eng. and Min. J.*, 1914, 787) precipitated mercury as hydroxide, dissolved the precipitate in standard potassium cyanide solution, and titrated the excess of cyanide against silver nitrate, using potassium iodide as indicator.

W. Böttger and R. Heinze (*Z. Elekt. Chem.*, 1916, **22**, 69) suggested two methods for determining mercury in small quantities, depending on the precipitation of mercury as diphenylcarbazine.

G. Adanti (*Boll. Chim. farm.*, 1916, **55**, 553) reduced mercury salts to metallic mercury by formaldehyde in the presence of potassium hydroxide (*cf.* E. Rupp, *loc. cit.* [ii]).

A. Tagliavini (*Boll. Chim. farm.*, 1917, **56**, 297) analysed solutions of mercuric cyanide and cyanate by adding sodium chloride and methyl orange and titrating against *N*/10 hydrochloric acid.

E. Votoček (*Chem. Ztg.*, 1918, **42**, 271) suggested that his method (*ibid.*, p. 257) for the determination of chlorides, bromides and cyanides by titrating with standard mercuric nitrate, with sodium nitro-prusside as indicator, might, conversely, be applied to the determination of mercury.

G. Jamieson (*J. Ind. Eng. Chem.*, 1919, **11**, 296) suggested a modification of Robertson's method (*loc. cit.*).

G. Hinard (*Amer. Chem. anal.*, 1920, [ii], **2**, 297) determines mercury in the presence of iron and vanadium. The mercury is precipitated as mercuric sulphide, which is subsequently oxidised with bromine water. The solution is rendered alkaline with caustic potash, excess of potassium cyanide is added, and the excess titrated with silver nitrate.

E. Bilman and K. Thanlow (*Bull. Soc. Chim.*, 1921, [iv], **29**, 587) described two methods for the determination of mercury based on the fact that allyl alcohol reacts with mercuric salts to give a hydroxide which is so feebly basic that it does not redden phenolphthalein. The hydroxide reacts with potassium bromide to liberate an equivalent amount of potassium hydroxide, which is titrated against standard acid.

Jellinek and Krebs (*Z. anorg. Chem.*, 1923, **130**, 263) and Jellinek and Kühn (*id.*, 1924, **138**, 109) determined mercury in mercuric chloride by titrating it against potassium cyanide, using phenolphthalein as indicator, and obtained results which were 3 per cent. too low. E. Rupp (*Z. anorg. Chem.*, 1925, **144**, 313) showed that these low results were due to the potassium cyanide being impure.

E. J. Kraus (*Chem. Ztg.*, 1926, **50**, 281) dissolved freshly precipitated mercuric sulphide in hydrochloric acid and iodine, and titrated the excess of iodine against thiosulphate.

E. Zintl and Rienacker (*Z. anorg. Chem.*, 1926, **155**, 84) determined mercury in the presence of salts of other metals by reducing the mercuric salts to metallic mercury with titanous chloride in hot acetic acid solution containing ammonium chloride and a bismuth salt as carrier, the end-point being determined potentiometrically.

Methods are suggested for the determination of mercury in small quantity, by (1) H. S. Booth, N. E. Schreiber and K. G. Zwick (*J. Amer. Chem. Soc.*, 1926, **48**, 1815), (2) P. Dennis (*Ann. Méd. légale*, 1921, **1**, 348), (3) A. Stock and R. Heller (*Z. angew. Chem.*, 1926, **39**, 466), (4) A. Stock and E. Pohland (*Z. angew. Chem.*, 1926, **39**, 791) (colorimetrically).

No reference in literature has been found in which stannous chloride has been employed for the volumetric determination of salts of mercury. N. A. Tananaeff (*Z. anorg. Chem.*, 1924, **133**, 372) suggested a spot test for the detection of mercury and tin, but did not develop his method for a quantitative determination.

FREE MERCURY IN COMMERCIAL PRODUCTS.—When attempting to determine free mercury in commercial products by converting it into mercuric bromide, Dunncliff and Lal (*ANALYST*, 1927, **52**, 329) failed to determine the mercuric bromide by any volumetric method. In connection with another problem the methods to be described were devised for the volumetric determination of mercuric chloride in neutral or hydrochloric acid solutions. They fail with mercuric bromide, but this compound in solution or suspension in water may be quantitatively converted into the chloride by passing chlorine gas through the liquid.

The excess of chlorine is removed by warming on a water-bath and introducing a current of CO_2 -free air, and the resulting mercuric chloride may be determined volumetrically. Analyses carried out in this manner gave

Mercuric bromide.	Determined by the stannous chloride method described, after conversion into chloride.	Sulphide method.
Grms.	Grms.	Grms.
1.8216	1.818	1.822
	1.821	

These results indicate that the volumetric method could be applied to all the types of commercial products referred to in the previous paper (*loc. cit.*).

Any processes by which mercury is separated as sulphide may be adapted to the volumetric process by dissolving the sulphide in *aqua regia* and evaporating the solution to dryness on a water-bath with excess of hydrochloric acid, and so converting the sulphide into chloride. The results obtained are about 1 per cent. low, owing to the loss of some mercuric chloride during the evaporation.

EXPERIMENTAL.—(1) Stannous chloride solution was prepared and standardised as described by E. Knecht and E. Hibbert ("New Reduction Methods in Volumetric Analysis," p. 17). The solution was stored in an atmosphere of carbon dioxide in an apparatus similar to that used for the storage of titanous chloride (*id.*, p. 63).

(2) Titanous chloride solution was prepared and standardised as described by Knecht and Hibbert (*loc. cit.*, p. 62). The solution of titanous chloride shows a continuous fall in strength on standing, and it is necessary to standardise the solution each day before use.

(3) Iron alum solution was made by boiling 48.20 grms. of pure ferric ammonium sulphate with strong hydrochloric acid and making the solution up to 1 litre. It was standardised against titanous chloride.

METHOD.—In the earlier part of the investigation an excess of standard $N/4$ stannous chloride was added to a mixture of 10 c.c. of mercuric chloride and 10 c.c. of a 25 per cent. solution of Rochelle salt, which was used to prevent the oxidation of stannous chloride by air. The precipitate of mercury so formed was allowed to settle in a vessel, through which a slow current of washed carbon dioxide was passed continuously. The clear supernatant liquid, which contained excess of stannous chloride, was pipetted into an excess of a hot solution of standard ferric alum, and the excess of ferric alum titrated back against titanous chloride. From the amount of ferric iron so reduced the corresponding quantity of stannous chloride was calculated, and, by difference, the amount of stannous chloride used in precipitating mercury from mercuric chloride. Calculation was facilitated by stating the strength of all solutions in terms of mercuric chloride and mercury.

The results obtained were generally very high, and sometimes were as much as 25 per cent. in excess of theory. These high results were found to be due to the

presence of a considerable excess of free hydrochloric acid in the stannous chloride solution, which must therefore be neutralised if the process is to succeed.

A mixture of 20 c.c. of stannous chloride with 20 c.c. of a 25 per cent. solution of Rochelle salt was neutralised with sodium bicarbonate. If the solution is not neutralised, the mineral acid in the original stannous chloride or that existing in the titanous chloride causes the separation of sparingly soluble potassium hydrogen tartrate, which is liable to interfere in the titration (*cf.* Knecht and Hibbert, *loc. cit.*, footnote, p. 7).

The results obtained were more encouraging and showed an error of about +5 per cent. To avoid the error induced by the separation of the sparingly soluble potassium hydrogen tartrate, sodium tartrate was used in place of Rochelle salt, and, after the conditions favourable for the reaction to proceed quantitatively had been studied, the following method was found to give the most accurate results:—

I. A measured volume of stannous chloride is mixed with an equal volume of a 25 per cent. solution of sodium tartrate in an open-mouthed graduated cylinder, through which a constant current of carbon dioxide is passed. The hydrochloric acid is then neutralised with a calculated amount of sodium bicarbonate, and the volume made up to 80–90 c.c. The contents are vigorously stirred (still in an atmosphere of carbon dioxide), and the solution standardised by the ferric alum and titanous chloride method (*vide supra*).

II. Process I is repeated and 10 c.c. of the mercuric chloride solution added to the neutral stannous chloride, and the whole made up to the same volume as in I. The solution is then quickly filtered through a Gooch crucible provided with a double layer of barium sulphate filter paper and asbestos, into a burette in an atmosphere of carbon dioxide, as shown in the figure. Ten c.c. of the filtrate are added to an

excess of a hot solution of standard ferric alum (water-bath), acidified with hydrochloric acid (to facilitate the reduction of ferric iron to ferrous), and the excess back-titrated against titanous chloride. Table I shows the results obtained by the above method.

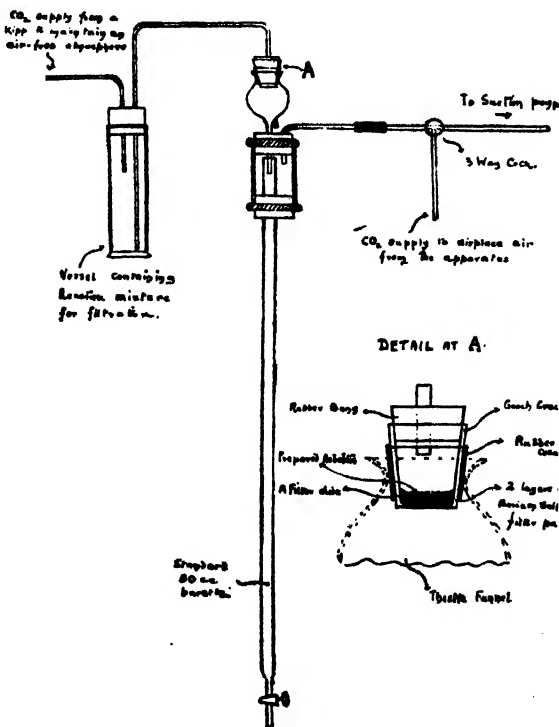


TABLE I.
Strength of Mercuric chloride in grms. per litre.

	Observed.	Taken.	Approx. normality.	Error. Per Cent.
I.	(a) 34.22	34.002	N/8	(a) +0.5
	(b) 34.00			(b) 0.0
II.	(a) 27.04			(a) -0.22
	(b) 27.14	27.100	N/10	(b) +0.14
	(c) 27.04			(c) -0.22
III.	(a) 13.60			(a) +0.29
	(b) 13.56	13.560	N/20	(b) 0.00
	(c) 13.55			(c) -0.07
IV.	(a) 9.01	9.032	N/30	(a) -0.21
	(b) 9.04			(b) +0.11
V.	(a) 6.80			(a) +0.44
	(b) 6.76	6.776	N/40	(b) -0.14
	(c) 6.76			(c) -0.14
VI.	(a) 5.42	5.420	N/50	(a) 0.00
	(b) 5.45			(b) +0.55

The stannous chloride and titanous chloride solutions require standardisation each day to obtain accurate results.

ALTERNATIVE METHOD.—A second method for the determination of mercuric chloride in solution, giving results of corresponding accuracy, has also been used. In this case, also, it is necessary to filter off the metallic mercury. The stannous chloride solution is neutralised as before. Mercuric chloride solution is added, and, after complete reduction has taken place, is made up to a known volume and filtered through the Gooch crucible into the burette. A known volume of the filtrate is run into standard iodine solution more than sufficient to oxidise the stannous chloride in the filtrate, and the excess of iodine titrated against $N/20$ sodium thiosulphate.

The degree of accuracy is about the same as in the first method. The two essentials for success are exclusion of air at the proper time and the separation of the metallic mercury from the solution to be titrated.

Table II gives some values obtained by this method.

TABLE II.
Strength of Mercuric Chloride in
grms. per litre.

	Observed.	Taken.	Error Per Cent.
I.	27.03	27.10 = $N/10$	-0.26
II.	13.52	13.55 = $N/20$	-0.22
III.	5.45	5.42 = $N/50$	+0.55

From Tables I and II it is seen that the range of concentrations over which these methods are valid is considerable, but we suggest that they should not be relied upon for concentrations lower than $N/40$.

Official Appointment.

Mr. HAROLD EDWARD MONK, B.Sc., F.I.C., as Public Analyst for the County Borough of Salford (to date from July 1st, 1929).

Notes.

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE KREIS REACTION AS A METHOD FOR THE DETECTION OF INCIPIENT RANCIDITY IN CACAO BUTTER.

CACAO butter being one of the most stable of the natural fats, rancidity seldom troubles the chocolate manufacturer. However, it would be an advantage here, as in other industries, to be able to detect incipient rancidity before the senses definitely indicate that a change has taken place.

The chemical literature was searched for a suitable test; the Kreis reaction, having been fairly fully investigated, and apparently approved, seemed to have possibilities.

The Kreis test (*Verhandlungen der Naturforschenden Gesellschaft in Basel*, 1903-04, 15, 225) consists in shaking the fat with strong hydrochloric acid and a 1 per cent. ethereal solution of phloroglucinol. A rancid fat should give a red or pink colour, the depth of which is proportional to the degree of rancidity. Kreis ascribed the reaction to the presence of aldehydes and ketones in the decomposing fat.

Winckel (*Z. Nahr. Genussm.*, 1905, 9, 90) stated that the test was valueless; it condemned oils and fats which were apparently fresh and sweet, in which even incipient rancidity would not be expected. Moreover, the test is not specific, since the reaction is given by ketones and aldehydes which do not occur in rancid fat.

After testing many hundreds of samples at the Washington Meat Inspection Laboratory the following conclusions were reached (Kerr, *J. Ind. Eng. Chem.*, 1918, 10, 471; *ANALYST*, 1918, 43, 327):—(1) All rancid fats react to the Kreis test. (2) The intensity of the reaction is roughly proportional to the degree of rancidity. (3) Fresh sweet fats do not give the reaction, except in certain special cases, *e.g.* crude cottonseed oil (the substance causing the reaction can be removed by refining with caustic soda). (4) The Kreis test is too delicate as a criterion of rancidity. (5) The Kreis test is not specific, but is given by aldehydes and ketones other than those occurring in rancid fat, by most essential oils, by crude cottonseed, and probably other crude oils.

Kerr's method, as modified by Swanger and Marsh and used at the Meat Inspection Laboratory, is as follows:—Ten c.c. of the oil or melted fat are placed in a large test-tube (8 in. \times 1 in.) and 10 c.c. of strong hydrochloric acid (sp. gr. 1.19) added. A rubber cork is inserted, and the tube shaken violently for about 30 seconds. Ten c.c. of a 0.1 per cent. ethereal solution of phloroglucinol are

added, and the tube shaken as before. On standing, to permit separation, a rancid fat gives a red or pink acid layer.

Kerr and Sorber (*J. Ind. Eng. Chem.*, 1923, 383) deal with the characteristics and causes of rancidity and give a number of more or less cumbersome methods for its detection. In reviewing the Kreis test they say "it is the most valuable and generally applicable."

In view of these favourable opinions I decided to investigate the suitability of the Kreis test as standardised for use at the Washington Meat Inspection Laboratories.

Supplies of rancid cacao butter were difficult to obtain, and all the commercial samples examined failed to give the reaction. We had, however, several old laboratory samples which were obviously very rancid and absolutely unpalatable. None of these specimens gave a positive reaction.

In the original Kreis reaction a 1 per cent. ethereal solution of phloroglucinol is recommended, as against the 0.1 per cent. of Kerr's modification. On changing the test solution to the original concentration no available genuine cacao butter reacted to the test, but a sample of cacao shell butter (which was at least 8 years old) gave a faint positive reaction. This fat was obviously very rancid. Diluted with an equal quantity of fresh sweet cacao butter the mixed fat, although still repulsive to the taste, failed to give the Kreis reaction.

In order to investigate the test in greater detail a graded series of rancid cacao butters was required. Use was made of the fact which we had known for some time, that the radiations from a mercury vapour arc lamp rapidly turn cacao butter rancid.

Quantities of 150 grms. of finest cacao butter were melted and poured into 250 c.c. glass beakers ($3\frac{1}{4}$ in. high \times $2\frac{3}{4}$ in. diameter). The depth of the fat layer was 2.1 in., and the upper surface $4\frac{1}{2}$ in. below the mercury vapour arc.

The beakers of fat were exposed for periods ranging from 5 minutes to 8 hours to the radiations from the mercury vapour lamp, the uroxameter value of which for the period of the test had an average value of 32 (*cf. J. Soc. Chem. Ind.*, 1925, 44, 453r). It seems reasonable to assume that the degree of rancidity will vary with the time of exposure to the lamp.

The Kreis test was tried on all the cacao butters prepared as above. Nine members of the Laboratory staff were asked to remark on the slightest evidence of rancidity.

The following observations were obtained:—

No.	Exposure to Mercury vapour arc. Minutes.	Temperature at start. °C.	Temperature at end. °C.	No. of the 9 observers who recorded fat as rancid.	Kreis reaction.
1.	0	32	—	2	Negative
2.	5	32	32	1	"
3.	10	32	34	1	"
4.	15	32	36	1	"
5.	30	32	39	2	"
6.	60	32	41	6	"
7.	120	32	41.5	6	"
8.	240	32	45.0	9	"
9.	480	32	49.0	9	Positive

It will be observed that the Kreis reaction only differentiates one of these fats as being rancid. Taste and odour throw out four fats as rancid by large majorities, in two cases without a dissenting vote.

Whilst I am aware that a fat in which rancidity has been produced under other conditions than the above may contain different decomposition products, yet in view of these tests and the fact that none of the cacao butters which had gone rancid under ordinary conditions gave the reaction, I conclude that the Kreis reaction as a means of testing for incipient rancidity in cacao butter is useless. In sensitiveness it does not approach the faculties of smell and taste of the ordinary observer.

I wish to thank Mr. A. W. Knapp, F.I.C., for help and suggestions, and Messrs. Cadbury Bros., Ltd., Bournville, in whose laboratories the work was carried out, for permission to publish this note.

T. H. COOKE.

DYES AS AN INDICATION OF ADULTERATION IN BUTTER.

IN cases where butter is suspected to be adulterated with margarine it is usual to carry out qualitative tests for cottonseed oil and sesame oil, in addition to other tests. Where the amount of margarine added is small, say, 10 per cent., the amount of cottonseed or sesame oil contained might only be about 1 per cent. according to the percentage of oils present in the margarine used, and the tests, in consequence, are of little value. It is well known that 10 to 15 per cent. of a margarine of a certain composition can easily be added to butter without the adulteration being detected by the Reichert-Wollny and Polenske methods, and the test to be described affords a useful indication of possible adulteration, or of the necessity for further investigation.

All samples of butter and margarine which pass through this laboratory are tested for prohibited colouring matters. It was found during these tests that 97 to 98 per cent. of the margarines examined contain a dye which is extracted by ammonia, whilst, with the majority of butter samples (94 to 95 per cent.), no colour is extracted by ammonia, and in cases where colour is shown, the colour is usually slight. To carry out the test, about 10 ml. of fat are shaken in a boiling tube with about 10 ml. of petroleum spirit and 10 ml. of 3 per cent. ammonia solution. The appearance of a coloration in the aqueous layer when butter fat is examined is an indication of possible adulteration with margarine.

Recently it was necessary to examine a series of butter samples which were suspected of adulteration with small percentages of margarine. Out of ten butters examined, the only sample which from the figures could be definitely described as genuine was also the only sample to give a colourless ammoniacal layer. The test described is obviously not a definite one, either negatively or positively, but may occasionally be helpful, as the presence of 10 per cent. of a dyed margarine is easily shown. The dye used in margarine appears to be of the same nature in all these samples. Thus it is extracted with *N*/100 sodium hydroxide solution, giving a yellow solution (*cf.* Nicholls, *ANALYST*, 1927, 52, 588). On applying Test A (*id.*, 589), the soda solution becomes pinkish-yellow, with a doubtful coloration of the ethereal layer. The weak alkaline solution is *not* decolorised by dilute acid.

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D. HENVILLE.
W. M. PAULLEY.

Notes from the Reports of Public Analysts.

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM.

ANNUAL REPORT OF THE CITY ANALYST FOR 1928.

IN presenting my twenty-sixth and last annual report I think that it will be of interest to review the steps which have been taken to prevent adulteration in Birmingham during the past half century.

In 1861, Dr. Alfred Hill was appointed Borough Analyst by the Town Council for one year, and was re-appointed the next year, in spite of an amendment that the office should be abolished. In 1863 he was required to undertake some sanitary work in addition to his analytical duties, and in 1872 he was appointed Medical Officer of Health, as well as Borough Analyst.

Unfortunately no records of the earlier years are extant, but from 1873 Dr. Hill's records and reports are available, and my personal knowledge of the working of the Food and Drugs Acts dates back to 1885.

In comparing the adulteration figures over a series of years, adulteration with preservatives has been dealt with separately, and, so far as possible, present-day standards have been applied to all the samples. For the last twenty years the "Comparative Adulteration Figure" (*i.e.* the number of vendors of adulterated samples for each 100 samples bought) has been used, instead of the percentage of adulteration; this figure depends much less on varying conditions of sampling. In 1908 to 1918 this figure was 3·4, and in the last decade it fell to 2·4.

In the period 1873–1878 twenty-eight per cent. of the samples were milk; in the last period they were 54 per cent. For fair comparison, the relation of the numbers of the various articles analysed should be similar for each period. A correction of the percentage of adulteration has been made by calculating the number of adulterated samples for 100 samples, made up of 52 milks, 9 butters, 2 spirits, 5 drugs, and 32 other articles. This figure gives the percentage of adulteration with standard sampling.

In the following table the figures for England and Wales and for London are calculated from data given in the annual reports of the Local Government Board from 1876 to 1913, and from those of the Ministry of Health from 1919 to 1927. These figures include a certain amount of adulteration by means of preservatives, and the only correction that can be applied to them is that to standard sampling.

	Percentage of Adulteration with Standard Sampling.			Total Number of samples per year per 100,000 persons living in Birmingham.
	England and Wales.	London.	Birmingham.	
1873— ..	—	—	40·6	30
1879— ..	13·8	15·5	20·6	127
1889— ..	9·9	13·9	12·7	216
1899— ..	8·6	10·6	7·9	276
1909— ..	8·3	8·7	7·1	438
1919–1928 ..	6·4*	4·5†	4·6	481

* 1919–27 only.

† 1920–27 only.

The above table shows that the average percentage of adulteration in Birmingham during the 56 years fell from 40·6 to 4·6. During the 49 years the figure for England and Wales fell from 13·8 to 6·4, and that for London from 15·5 to 4·5.

In the decade commencing 1879 the proportion of adulteration in Birmingham was distinctly higher than the other figures, but in later years the disproportion diminished, and now Birmingham is better than the average of the country and similar to London; owing to the difference in administrative conditions, the comparison of the figures must not be pressed.

In the first six years of the table the annual average of samples taken was 30 per 100,000 persons living in Birmingham; in the last decade this number had increased to 481. The proportion in England and Wales for 1927, the last available year, was 317.

ADULTERATION WITH PRESERVATIVES.—Before 1896, samples of ale and beer were tested for excess of common salt, but apart from this no examination for preservatives was made. In that year Dr. Hill, at the request of the Public Health Committee of Birmingham, investigated the question of the use of preservatives in food.

Boric acid was detected in milk, butter, cream, bacon, pork pie, vinegar, and other foods. Salicylic acid was found to be present in jam, cream, sherry and ipecacuanha wine. Formic aldehyde was also detected in milk.

As a result of these investigations, Dr. Hill publicly advocated prohibition of the use of preservatives in food. At a conference of the Sanitary Institute held in Birmingham in 1898, he took that subject for his presidential address to one of the sections, and the next year gave a paper before the Incorporated Society of Medical Officers of Health, and a resolution was passed deprecating the use of preservatives in foods. In the same year he gave evidence as representative of that Society before the Departmental Committee which enquired into the use of preservatives and colouring matters. In 1901 that Committee made a report and recommended limitation or prohibition of preservatives in food. Unfortunately, no legislation resulted, and, although prosecutions for preservatives in milk were instituted under the Sale of Food and Drugs Acts, it was not until 1912 that the Milk and Cream Regulations definitely prohibited the use of preservatives in milk.

In 1923 another Departmental Committee was appointed, and that Committee finally reported in 1924. In the following year the Public Health Preservatives, etc., in Food Regulations were passed.

Since the passing of these Regulations various foods have been tested for the presence of sulphur dioxide; in most cases with negative results. Samples of pearl barley contained up to 120 parts of sulphur dioxide per million, and samples of ginger up to 3000 parts per million. One sample of crystal mints contained nearly 1000 parts per million.

MILK.—In 1900 no less than 11·4 per cent. of the samples examined contained either boric acid or formaldehyde. In several cases 6 to 9 grains of boric acid per pint were present, and in one case 16 grains per pint were found. In the period 1896–1902 there were 7 prosecutions for boric acid in milk, and only 2 cautions for formaldehyde. In 168 cases no action was taken, since the Public Health Committee was not well supported by the magistrates. In one instance, in which boric acid and formaldehyde were both present, as well as 14 per cent. of water, the defendant was only ordered to pay 5s. costs. The vendor of a milk containing 16 grains of boric acid per pint was only fined 2s. 6d.

In 1897, when a vendor was cautioned for preserving his milk with formaldehyde, he said that he intended to go on using the preservative, and that the

Committee could not stop him. Unfortunately that statement was correct, as at that time while formaldehyde could readily be detected in milk, there was no available means for determining it, and prosecutions could not be instituted unless the amount of adulterant was stated.

As vendors were being prosecuted for the use of boric acid and not for formic aldehyde, the latter preservative became more popular. Between 1897 and 1903 the proportion adulterated with boric acid fell from 5.5 per cent. to 1.5 per cent., whilst milks containing formaldehyde increased from 3.3 per cent. to 6.4 per cent.

In 1902 I devised a method for the determination of formic aldehyde, and in the next year there were successful prosecutions for this preservative, which were among the earliest in the country.

The results of the action taken in the second period resulted in the fall of preservative adulteration to 0.2 per cent. in the third period; since 1915 the adulteration of milk with these preservatives has been very unusual.

CREAM.—Before the issue of the Regulations of 1912 only 17 per cent. of the samples of cream were free from boric acid. Each subsequent period showed an improvement, and last year nearly all the samples of cream were free from boric acid.

Only 64 per cent. of the preserved creams bought under the 1912 Regulations were correctly labelled, but during the last three years the proportion increased to 84 per cent. When creams had been preserved with boric acid there was a decided decrease in the proportion used. In 1913–1916, 66 per cent. of the samples did not contain more than 28 grains per pound. In the next period the proportion improved to 98 per cent.; on the other hand, samples containing over 35 grains per pound decreased from 12 per cent. to 1 per cent. in the two periods. The largest amounts detected in a period fell from 70 to 7 grains per pound.

BUTTER.—Butters were first tested for boric acid in 1896, and Dr. Hill reported all samples containing this preservative as adulterated. Fourteen vendors were cautioned for samples containing from 6–25 grains of boric acid per pound. This action was, however, in advance of the times, and no further action was taken until 1898, when a vendor was fined for 70 grains per pound. Other prosecutions followed, and in the years 1898–1904, 13 vendors were prosecuted for samples of butter containing from 55–112 grains of boric acid per pound, and paid fines and costs amounting to £24. There were also 9 prosecutions for samples of butter which contained boric acid and also an excess of water, for which fines and costs amounting to £29 were paid by vendors.

During each decade 68 to 69 per cent. of the samples were free from boric acid. From 1899 to 1905 no less than 11.9 per cent. of the preserved samples contained over 35 grains of boric acid per lb., but the prosecutions during that period had a salutary effect, for in the next decade only 1.9 per cent. exceeded that figure, and after that very few samples contained more than 35 grains per lb.

SAUSAGE.—In 1908, 44 per cent. of the samples were free from boric acid, but in 1922–6 only 14 per cent. were free. Since Preservatives Regulations prohibiting boric acid came into force, in 1927, all the samples examined have been free from this preservative.

Besides the increasing use of preservative, the amount used was also greater. In 1908, 37 per cent. contained under 14 grains per pound, and 16 per cent. 35 grains and over. In 1922–6 samples containing the smaller proportion of preservative had decreased to 28 per cent., and the larger increased to 22 per cent. There have been no prosecutions in Birmingham for the presence of boric acid in sausage.

Three of the 10 samples bought as "sausage" last year were adulterated, containing from 100 to 290 parts of sulphur dioxide per million. The last one,

after frying for a quarter of an hour, contained 240 parts per million, showing that little of the preservative was dissipated by cooking.

BEER.—In the first sixteen years (1873–1888) 3 per cent. of the samples contained more than 70 grains of chlorides. In the next twenty years the proportion increased to 10 per cent., in the next decade (1909–1918) 6 per cent. were above the limit, and in the last decade the proportion fell to 1 per cent.

COLOURED AND BLEACHED FOODS.—In 1874 three vendors were fined for sweets known as “Birds’ Eggs,” which were coloured yellow with chromate of lead, but no similar adulteration has been detected since. In 1907, 11 samples of preserved peas and beans contained copper varying from 0.1 to 1.0 grain of metallic copper per pound. In 3 samples the presence of a “small quantity” of copper was declared on the label, but not in the case of the larger amounts. The two samples of preserved peas examined last year were found to be free from copper.

The colouring of milk has never been common in Birmingham. In the decades commencing 1888 and 1898, 1.4 per cent. of the milks were coloured. In 1904 the Committee sent out a warning circular on the matter to milk dealers, and in the next ten years only 0.3 per cent. of the samples were coloured.

In the 5 years commencing 1910, 57 per cent. of the Birmingham samples of flour analysed contained from 2 to 10 parts per million of sodium nitrite as the result of bleaching. Before 1905 flour was sold in its natural state, but gradually much “flour” was withdrawn and bleached flour sold in its place without any notice being given to the consumer of the substitution that had been made.

Last year three samples of sultanas were examined. The palest, which was the highest priced, had been bleached with sulphur dioxide, but the other two were free from it. This appears to be another case in which an article, inferior because of containing preservative, is considered superior in colour, and is sold at a higher price because it has been artificially bleached.

PEARL BARLEY.—During the years 1910–1928, 707 samples were examined, and of these 25 bought in the years 1913 and 1914 were adulterated by facing either with talc or rice flour. Fourteen samples had been faced with talc, 0.2–0.7 per cent. being present. Nine samples had been faced with 0.5–2 per cent. of rice flour, and 2 samples were faced with both rice and talc. Cautions were given to retailers, wholesale dealers and a London wholesale house, and all the samples examined in subsequent years have been unfaced.

This is apparently another example of adulteration to give increased whiteness. In later years bleaching by sulphur dioxide may have taken the place of facing previously used. Last year 6 samples contained from 10–120 parts of sulphur dioxide per million. Its presence is prohibited by the Preservatives Regulations of 1925.

In the years 1912 to 1920, 32 per cent. of the samples contained over 1.1 per cent. of ash, but in the next eight years only 12 per cent. exceeded that figure, indicating a great improvement.

There has also been improvement in the cleanliness of the samples of pearl barley. In the six years, 1918–23, 55 per cent. of the samples contained mites, either alive or dead, but in the following five years the percentage fell to 30. It is obviously advisable that pearl barley should be washed before use.

Of the samples of barley examined in England and Wales during the years 1920–7, 2.8 per cent. were reported adulterated.

VINEGAR.—In 1893 four samples of vinegar were submitted to Dr. Hill for analysis in one day, and were found to be artificial vinegar. Prosecutions ensued, and the vendors were fined. One of the vendors appealed to Quarter Sessions, and, after a lengthy hearing, the appeal was dismissed with costs. Since that

date the sale of artificial vinegar in Birmingham has been unusual, only 2·4 per cent. of the samples being thus adulterated, and in some cases duplicate samples were obtained from one vendor.

One vendor, last year, who sold artificial vinegar both as vinegar and malt vinegar, was defended by the makers of the vinegar. The vendor, who was a foreigner, stated that she did not hear the word "malt," but her evidence was unconvincing. I gave evidence that either vinegar or malt vinegar should be prepared by fermentation and acetification, and that artificial vinegar was simply prepared by diluting and colouring acetic acid. I was shown a label which was said to have been on the cask from which the article was taken, but not visible to the purchaser. As this label stated "Pure Vinegar," I said that it was a false one.

The defence also suggested that a case at Leeds Assizes had settled, for the whole of the country, that artificial vinegar could be sold as vinegar. This was a case in which the makers of the artificial vinegar claimed damages for libel from a vinegar brewery company. All this case settled was that the artificial vinegar makers were libelled; the jury assessed the damages as one farthing without costs. The magistrates imposed a fine of £1.

BAKING POWDER.—In 1894 an appeal case decided that baking powder was not legally a food, although a large proportion of it was of a starchy nature. In 1899 the definition of "food" was enlarged to include "any article which ordinarily enters into or is used in the composition or preparation of human food." The necessity of samples being taken under the Sale of Food and Drugs Act was shown by the fact that in the next year 6 of the 19 samples contained alum, the proportion present varying from 13–30 per cent., and the vendors were prosecuted for selling an article injurious to health. One of these samples was marked "Prize Medal Baking Powder," and the label on another actually claimed that the article would make bread more digestible, in spite of the presence of 25 per cent. of alum.

Since that year 57 samples have been analysed. In 1916 one sample contained 12·4 per cent. of calcium sulphate and 25 parts of arsenic per million, and a second sample of the same make had a similar composition. The presence of these impurities was due to the acid calcium phosphate used being of inferior composition.

In 1922 one sample contained an excess of calcium sulphate. In 1927–8 four samples were of inferior quality, yielding 3·4 to 4·6 per cent. of carbonic acid gas, while samples of good quality yielded from 6·0 to 9·4 per cent. The practical value of the powder is proportional to the amount of carbonic acid gas yielded by it. Last year a manufacturer who was cautioned undertook to increase the strength of his powder.

J. F. LIVERSEEGE.

Legal Notes.

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

AMMONIATED TINCTURE OF QUININE.

At Thames Police Court, a pharmacist was summoned for selling on September 28th, 1928, ammoniated tincture of quinine which was deficient in ammonia to the extent of 15·8 per cent. The pharmacist stated that he had had one pint of the tincture in stock for three days only, and that it must have been received by him at practically the same strength as he had sold it.

The analyst for the defence agreed with the figures of analysis, but regarded the loss of ammonia as negligible and due to loss in filtration during manufacture and in opening the bottle while dispensing. Similar evidence was given by the

analyst to the wholesale firm which supplied the tincture. The solicitor for the defence stated that the British Pharmacopoeia gave no tests for the strength of ammoniated tincture of quinine, and that the theoretical composition did not constitute a standard. He quoted the figure of "about 0.9 per cent. w/v of absolute ammonia" given in Squire's Companion to the British Pharmacopoeia, and produced a pamphlet described as "Local Government Dept., Revised Standards for Pharmacopoeial Preparations," which, he stated, contained a standard for ammonia in the tincture.*

Rebutting evidence was given for the prosecution by Mr. D. Henville, Public Analyst for Stepney, who explained that tests regulating the composition of each constituent of ammoniated tincture of quinine were definitely detailed in the British Pharmacopoeia, that the manufacture of the tincture consisted in the simple admixture of these standard constituents, followed by filtration, and that it was only reasonable to assume that the resulting product would closely approximate in composition to the theoretical standard.

Results of a series of experiments made to ascertain the amount of loss of ammonia caused by dispensing a pint of the tincture in small quantities over a period of three days were given. This loss amounted to less than 1 per cent. The witness did not accept the minimum standard in the pamphlet produced.

Further evidence for the prosecution was given by Mr. R. A. Cripps, F.I.C., who gave figures showing the small loss of ammonia during dispensing and during manufacture under various conditions of filtration. The experiments on which this evidence was based, were as follows:—

	Loss of original Ammonia Per Cent.
After filtration in uncovered filter	2
" " " lightly covered filter	Nil
(Loss due to experimental error would not exceed 0.008 per cent.)	
After exposure in open bottle for 19½ hours	13.5
" " " beaker " 2½ " at 15° C.	12.5
" " " " " " 18° C.	18.0
(In draught from open window)	
On serving out ½ to 1 oz. from 12 oz. bottle containing 11 ozs. of tincture, last portion poured out	0.5
2nd test	0.7
Total loss, sample "A" bad conditions of filtration, serving out 17 times	2.5
Total loss, sample "B" usual conditions, and serving out 17 times	0.7

The case was adjourned a number of times, and at the last hearing, on March 25th, the magistrate (Mr. Cairns) fined the defendant £2, with £15 15s. costs.

SULPHUR DIOXIDE IN GROUND GINGER.

ON May 29 an adjourned summons against a trading company was heard at West Ham, London, for the sale of ground ginger containing 1564 parts of sulphur dioxide per million.

The Medical Officer for West Ham (Dr. Collins) said that he was not pressing the case, but the presence of this amount of sulphur dioxide in the ginger was contrary to the Regulations.

The solicitor for the defence said that the company took every precaution to assure themselves that all their goods complied with the regulations. After the

* No intimation as to the origin of this pamphlet was given, and the standard was a minimum figure only. It was later found that this pamphlet was a publication of the Irish Free State.

matter had been discussed at several meetings of the Spice Association, it had been decided that guarantees should be given, but it appeared that there was still controversy with the Ministry of Health. In India and Cochin, owing to the humidity of the moisture, a preservative had to be used during the drying of the roots, and they were then bleached with lime. The lime retained the sulphur dioxide, but in cooking it would disappear to a large extent. When the regulations first came into force the importation of this ginger from Cochin and India was stopped. The whole ginger roots could be sold as bleached ginger, but when powdered they could not be sold. The Company was perfectly innocent of any cognisance of an offence in this case.

Mr. St. John Morrow said that he understood this, and that the case would be met by the defendant company paying £1 as costs. There would be no conviction.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Copper Content of Plant and Animal Foods. C. W. Lindow, C. A. Elvehjem and W. H. Peterson. (*J. Biol. Chem.*, 1929, **82**, 465-471.)—The copper content of about 160 samples of common food materials has been determined by the modified Biazzo method, as outlined by Elvehjem and Lindow (*J. Biol. Chem.*, 1929, **81**, 435; *ANALYST*, 1929, **54**, 245). The copper content is calculated on the dry basis and fresh basis, and a table gives the results. The figures range from 0.1 mgrm. of copper per kilo of fresh celery to 44.1 mgrms. per kilo. of fresh calf liver. The classes of foods in descending order of their average copper content per kilo. of fresh material are :—10 nuts, 11.6 mgrms.; 4 dried legumes, 9.0 mgrms.; 19 cereals, 4.7 mgrms.; 8 dried fruits, 4.2 mgrms.; 4 kinds of poultry, 3.0 mgrms.; 17 kinds of fish, 2.5 mgrms.; 13 animal tissues, 1.7 mgrms.; 2 green legumes, 1.7 mgrms.; 11 roots, tubers, stalks and bulbs, 1.4 mgrms.; 14 leafy vegetables, 1.2 mgrms.; 27 fresh fruits, 1.0 mgrm.; and 10 non-leafy vegetables, 0.7 mgrm. The copper content of leafy vegetables does not place them in the pre-eminent position that they hold with reference to their iron content. A wide variation was found in the copper content of livers from different animals; calf liver was highest (44.1 mgrms.) and hog liver was lowest (6.5 mgrms.). The copper content of oysters was strikingly high (30.7 mgrms. per kilo.), and surpassed all the sea foods in this element. Unlike the data obtained for the iron content of salt water and fresh water fish (*J. Biol. Chem.*, 1928, **78**, 215; *ANALYST*, 1928, **53**, 444), the average figures for the copper content of the two groups are practically the same. A table shows that the degree of variation in the copper content of foods falling in the same class was less than that of either manganese or iron. There is a wide distribution of copper in food materials; no food examined was without this element. Certain milled cereals, such as polished rice and patent wheat flour, are very low in copper, as compared with the whole grain from which they were made.

P. H. P.

Copper Content of Feedingstuffs. C. A. Elvehjem and E. B. Hart. (*J. Biol. Chem.*, 1929, 82, 473-477.)—In a previous paper by Skinner and Peterson (*J. Biol. Chem.*, 1928, 79, 679) the manganese and iron content of 51 feeds was given. The same series has now been analysed for copper in order to compare the relative abundance and distribution of the three elements in the same feeds. Experiments were also carried out to determine whether or not fertilisation with copper salts would influence the copper content of the crop grown. The copper content of 47 common feeds is given. The average copper content of 42 of the feeds is 13.5 mgrms. per kilo of dry matter. The average iron and manganese contents of the same 42 feeds are 199.0 and 65.8 mgrms. per kilo. of dry matter, respectively. Therefore the average copper content of these feeds is one-fifth of the manganese and one-fifteenth of the iron content. Certain manufactured feeds are unusually high in copper, probably owing to contamination, e.g. gluten feed 89.5, and distillers' grain 38.4 mgrms. per kilo. of dry matter. The feedingstuffs arranged in ascending order of copper content are as follows:—Straws and stovers, hays and grasses, and seeds and seed products. Crops grown on a plot treated with copper sulphate at the rate of 50 pounds of the salt per acre, added in solution to insure uniform distribution, showed a small but definite increase in their copper content. In a single experiment, in which only lettuce was involved, the copper fertilisation was increased tenfold, i.e. 500 pounds of copper salt per acre were added, and an increased copper content of 148 per cent. was shown by the lettuce over that produced on untreated soil. Therefore the copper content of the crop can be increased within certain limits by fertilisation of the soil with a copper salt.

P. H. P.

Determination of Reducing Sugars, particularly of Glucose, by Alkaline Copper Solutions in the presence of Hydrocyanic Acid. H. Herissey and A. Chalmeta. (*Ann. Falsif.*, 1929, 22, 214-223).—The presence of hydrocyanic acid will cause a loss or even a total apparent disappearance of reducing sugars when determined in alkaline copper solutions, whether the determination is finished colorimetrically or gravimetrically, partly owing to combination of the reducing sugar in the alkaline medium with the hydrocyanic acid, and partly by formation of a double cyanide of sodium and copper from the cuprous oxide in alkaline solution. Hydrocyanic acid may be eliminated before the determination in simple cases either by heating (evaporating the solution to half the volume or to dryness and redissolving); or, in others, by passing through the solution a current of air for a prolonged period, or chemically by the addition of a very slight excess of silver nitrate, followed by filtration and addition of sodium chloride to remove any traces of silver salt. In the case of liquors obtained by hydrolysis of a glucoside by emulsin precautions are necessary, such as the effecting of certain preliminary separations before evaporation.

D. G. H.

Divinylglycol as the Cause of the Bitter Flavour of Wines suffering from Bitterness. E. Voisenet. (*Comptes rend.*, 1929, 188, 1271-1273.)—A

compound isolated from a Burgundy wine exhibiting the disease known as "bitterness," was found to consist of divinylglycol, which is doubtless formed from acrolein by the action either of the reductases normally present in wines or of a hydrogenase secreted by the "bitter" organism.

T. H. P.

Detection of Fruit Wine in Grape Wine by Means of Dibenzal-sorbitol.

C. von der Heide and K. Hennig. (*Z. Unters. Lebensm.*, 1929, **57**, 240-241.)—According to Werder (*Mitteilg. a. d. Gebiete d. Lebensmitteluntersuchung u. Hygiene*, 1928, **19**, 294) 100 c.c. of wine are boiled for 3 minutes with 10 grms. of active charcoal, filtered hot, and the filtrate and washings evaporated under reduced pressure (70° C.) to a colourless syrup. This is well shaken with 4 drops of benzaldehyde and 0.8 c.c. of 50 per cent. (by volume) sulphuric acid, and on the following day, diluted with 100 c.c. of water, when a white precipitate (dibenzal-sorbitol) indicates fruit wine. The authors consider it necessary to identify this precipitate, on account of the separation of other substances (*e.g.* gypsum) from grape wine. The precipitate is filtered on a sintered glass crucible, washed free of acid, dried with alcohol and ether, and extracted with benzene for 3 hours. This dissolves only the dibenzal-sorbitol, leaving the organic impurities (benzaldehyde, benzoic acid, glycerol, etc.). The solution is evaporated, and the residue recrystallised from benzene. It has m.pt. 162° C., whilst tribenzal-mannitol has m.pt. 213 to 217° C. (both uncorr.).

J. G.

Analysis of the Bitter Substances of Hops. **W. Windisch, P. Kolbach, and M. Winter.** (*J. Inst. Brew.*, 1929, **35**, 269-270.)—In the usual method of determining the α -bitter acid or humulone of hops by precipitating it from methyl alcoholic solution as lead salt, a slight excess of the dilute lead acetate solution (1 per cent.) must be used, but the precipitate is appreciably soluble in excess of the reagent, and more so in solutions containing other hop resins than in solutions of pure humulone. It is recommended that a series of test-tube trials be made with 2 c.c. of the resin solution, 2 c.c. of methyl alcohol, and varying amounts of lead acetate solution, these being heated for 5 minutes in a water-bath at 65-70° C. and filtered, and the filtrates tested with sulphide, so that the proper amount of the lead salt to use may be ascertained. For the actual analysis, 10 c.c. of the resin solution, 10 c.c. of methyl alcohol, and the requisite volume of lead acetate solution are heated together for 5 minutes in a gently boiling water-bath, and allowed to stand for 10 minutes before filtering, the precipitate being then washed 6 times with 5 c.c. portions of methyl alcohol, dried, and weighed. No oxidation of humulone to resinous substances occurs during this procedure, but even with extracts from fairly fresh hops the precipitate is apt to be slightly contaminated with resins. This may be ascertained from the weight of lead in 1 part by weight of the precipitate; the correct lead factor is 0.3653, but values varying from 0.360 to 0.364 were found for different samples of lupulin. Moreover, the humulone obtained by acidifying the precipitates gave iodine values of 147-149, the correct value being 151.3-151.5.

As hops age, the small inaccuracies indicated by the above figures become more serious, owing to the appearance of an excessive proportion of hard resins, which contaminate the lead humulate and, later, of other resinous decomposition products. Hard resins may be eliminated by extracting the hops with hexane, which dissolves only the soft resins and bitter acids. After protracted ageing, the hops contain a disturbing substance soluble in hexane, but this may be removed by shaking the extract with an aqueous phosphate buffer solution of P_H 6.4, the humulone being afterwards precipitated as usual. The humulone content furnishes the most trustworthy indication of the state of preservation of hops, as it undergoes far greater changes than the soft resin content found by extraction with petroleum spirit or hexane.

T. H. P.

Composition of Spinach Fat. J. H. Speer, E. C. Wise and M. C. Hart. (*J. Biol. Chem.*, 1929, **82**, 105–110.)—Sixty-eight kilos. of dried spinach were extracted with cold acetone, the extract obtained by concentration under nitrogen at reduced pressure dissolved in boiling alcohol, the insoluble material filtered off, the alcohol evaporated, the residue dissolved in ether and washed with 1 per cent. sulphuric acid, the free fatty acids removed, followed by removal of chlorophyll and its degradation products. The yield was 550 grms. of fatty acids, 47 per cent. of which were present as glycerides and 53 per cent. free. The solid acids weighed 26.5 grms. (separation not quantitative) consisting chiefly of palmitic and stearic acids, with 3 per cent. of cerotic acid. Of the 145 grms. of liquid acids recovered from the fractionation processes, at least 12.7 per cent. were linolenic, 24.7 linolic, and 26.3 per cent. oleic acids. Volatile acids, if present at all, were only so in traces.

D. G. H.

Glycerides of Chaulmoogra Oil. A. Bömer and H. Engel. (*Z. Unters. Lebensm.*, 1929, **57**, 113–147.)—To eliminate changes due to rapid atmospheric oxidation the oil was hardened in the presence of 0.1 per cent. of a 1 per cent. mixture of palladium and kieselguhr at 170 to 200° C. The hardened oil (m.pt. 27 to 28° C.), in which a ring double-bond had been satisfied with two hydrogen atoms, was optically inactive. As a result of a large number of fractional crystallisations from acetone and ether at about 0° C. curves were plotted showing the m.pt. and the weight of the fractions, and the presence of 79 per cent. of dihydro-chaulmoogro-dihydro-hydnocarpin (m.pt. 30.7° C., corr.), 13 per cent. of dihydro-hydnocarpo-di-dihydro-chaulmoogrin (m.pt. 42.2° C., corr.), and traces of a slightly soluble glyceride (possibly tripalmitin or a stearo-dipalmitin) was established. The results were checked by determinations of the saponification, iodine and acid values of the fractions, and by fractional precipitation of the fatty acids with magnesium acetate. The natural oil therefore contains the corresponding unsaturated glycerides chaulmoogro-di-hydnocarpin and hydnocarpo-di-chaulmoogrin in corresponding proportions, whilst the fatty acids of the hardened oil have the composition: 40 per cent. dihydro-chaulmoogric acid and 59 per cent. dihydro-hydnocarpic acid (*cf.* Dean and Wrenshall, *ANALYST*, 1921, **46**, 52).

Tridihydro-chaulmoogrin (m.pt. 51.0° C., corr.) was synthesised by the action of the lead salt of dihydro-chaulmoogric acid on tribromhydrin in the presence of xylene at 170 to 180° C. for 10 hours, and tri-dihydro hydnocarpin (m.pt. 39.2° C., corr.), di-dihydro chaulmoogrin (m.pt. 60.7° C., corr.), trilaurin and trimyristin were obtained in an analogous manner. Dihydrochaulmoogric and dihydro-hydnocarpic acids are three and four times more soluble in alcohol than stearic and palmitic acids, respectively. J. G.

Nitrobenzaldehyde as Reagent for Organic Medicines. H. W. Van Urk. (*Pharm. Weekblad*, 1929, 66, 429-435.)—The reagent consists of a 1 per cent. alcoholic solution of *o*-, *m*- or *p*-nitrobenzaldehyde to which dilute sulphuric acid is added until the acid strength is about 2 per cent. A little of the sample is heated or evaporated on the water bath with 5 to 10 drops of reagent, and a coloured residue obtained. The results are tabulated for numerous substances. Amino-compounds do not react, and the author's *p*-dimethyl-amino-benzaldehyde (*id.*, 1929, 66, 101; *ANALYST*, *infra.*) reaction should be used. Simple phenols and polyphenols react, whilst mandelic acid and homatropine do not, though tropic acid and atropine give a positive reaction. Salicylic acid gives no marked reaction with the *m*- or *p*-compounds, but salol reacts with all three. Other exceptions are the purines, pyridine derivatives, nicotine, papaverine, and cotarnine. The phenetidines, pyrroles, and alkaloids containing hydroxyl groups react. Narcotine reacts only with the *o*- compound, and hydrastine gives a negative reaction unless previously heated with hydrochloric acid. Morphine differs from codeine in that it gives a green colour with the *o*-reagent, if previously heated, instead of the yellow normally given by both substances, while the aqueous solution of the residue is brown instead of orange-yellow. In general, the three isomers behave similarly. J. G.

Microchemical Reactions of Piperine. M. Wagenaar. (*Pharm. Weekblad*, 1929, 66, 405-406.)—Piperine, $C_{17}H_{19}NO_3$, is a very weak base crystallising in badly-defined prisms, m.pt. 128° to 129° C., refractive index, 1.70 and 1.55 (Kley). It is insoluble in water, and soluble in ether, chloroform, and cold (1 in 30) or hot (1 in 1) alcohol. The acetate may be prepared in prisms about 1 mm. long by cooling a solution of a little solid piperine in the minimum amount of warm 30 per cent. acetic acid, and, if necessary, by salting out with sodium acetate. The alkaloid (50 m.grms.) is precipitated from a solution in a drop of acetone as fine needles, 100μ long, by the addition of a drop of water. J. G.

Microchemical Reactions of Physostigmine. M. Wagenaar. (*Pharm. Weekblad*, 1929, 66, 381-382.)—Physostigmine, $C_{15}H_{21}N_3O_2$, has strongly basic properties and crystallises in shining leaflets, m.pt. 102° to 103° C., refractive index 1.66 and 1.54 (Kley), slightly soluble in water, and readily soluble in alcohol, ether or chloroform. Sodium salicylate solution gives a precipitate with the sulphate of doubly refracting cubic or hexagonal crystals, 200μ in size, which may be obtained from super-saturated solutions by addition of ammonium sulphate. If the sulphate

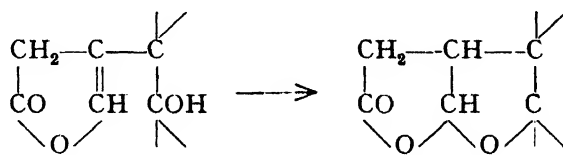
is acidified with dilute hydrochloric acid and a crystal of sodium bromide added, followed by a drop of gold trichloride solution, there is a brown-red precipitate. The limiting concentrations for these reactions are 1:200 and 1:500, and the smallest amounts detectable are 10 and 5 m.grms., respectively. J. G.

New Reactions of Cantharidin. H. W. Van Urk. (*Pharm. Weekblad*, 1929, 66, 313-317.)—(1) Cantharidin (0.1 mgrm.) is nitrated by evaporation with 5 c.c. of 50 per cent. nitric acid, and the residue reduced by the addition of two drops of a fresh solution of stannous chloride in 25 per cent. hydrochloric acid. After three minutes on the water-bath 1 drop of a 1 per cent. solution of sodium nitrite is added in the cold, the excess of reagent removed by urea, and a violet-red azo dye produced by the addition of a fresh 1 per cent. solution of α -naphthol in 10 per cent. ammonia. (2) The nitrated cantharidin is mixed with 10 drops of a 1 per cent. alcoholic solution of *p*-dimethyl-amino-benzaldehyde, and dilute sulphuric acid added till an acid strength of 2 per cent. is obtained. In the presence of 0.5 mgrm. of cantharidine a yellow-red residue is obtained on evaporation, and a yellow solution or precipitate on the addition of water. (3) David's test (*Pharm. Ztg.*, 1927, p. 56) may be used as a ring-reaction sensitive to 5 mgrms. of cantharidin by adding a layer of an alcoholic solution of vanillin to a solution of nitrated cantharidin in strong sulphuric acid, when an orange-red ring is obtained. Blank tests on the reagents should be made in the above cases, as these may yield yellow colorations (*cf. Pharm. Weekblad*, 1929, 66, 101). J. G.

An Impurity in Commercial Narceine which gives a Colour Reaction with Sodium Nitroprusside. J. J. L. Zwikker. (*Pharm. Weekblad*, 1929, 66, 445-449.)—The methylation of narcotine involved in the synthesis of narceine may result in the production of methyl narceine which gives a red colour in the Bitto sodium nitroprusside reaction (*cf. id.*, 1929, 66, 50). The test is carried out by the addition of 2 drops each of a 10 per cent. solution of reagent and 4 *N* sodium hydroxide solution to a solution of 50 mgrms. of narceine hydrochloride in 2 c.c. of water, and it is capable of detecting 2 per cent. of methyl narceine. These conclusions were confirmed by the methylation of pure narceine and by the extraction of the methyl compound from commercial narceine, followed by determinations of the m.pt. (234° C., corr.) and equivalent weight of the hydrochloride. J. G.

The Digitalis Glucosides. III. Gitoxigenin and Isogitoxigenin. W. A. Jacobs and E. L. Gustus. (*J. Biol. Chem.*, 1929, 82, 403-409.)—In a previous communication by Jacobs and Gustus (*J. Biol. Chem.*, 1928, 79, 553) the conclusion was reached that gitoxigenin is a $\Delta^{\beta,\gamma}$ -lactone like digitoxigenin and the related cardiac aglucones, but certain dissimilarities were observed in the derivatives of isogitoxigenin. It is now definitely shown that isogitoxigenin, like the other *iso*-compounds, is a lactone or the lactol form of a hydroxyaldehyde. Contrary to the former belief, isogitoxigenin when saponified displays great stability towards alkali. Renewed study has resulted in a much improved yield of the *iso*-compound from gitoxigenin. Re-investigation of the preparation and composition of the

so-called isogitoxigenonic methyl ester has confirmed the formula, $C_{24}H_{34}O_6$, previously reported. This ester only consumes 1 equivalent of 0.1 N alkali when saponified by the method which decomposed both ester and lactone group in the case of the analogous isodigitoxigenin, isostrophanthidin, etc., derivatives, but by the use of stronger alkali and higher temperature, a relatively resistant lactone group can be detected in the isogitoxigenin derivative. Therefore, this substance is a ketolactone ester, and, in conformity with the analogous substances obtained from the other iso-compounds, should be called *isogitoxigenic methyl ester*. The acid obtained on oxidation with hypobromite of isogitoxigeninic acid (prepared by saponification of isogitoxigenin) was given the incorrect formula $C_{21}H_{30}O_6$. It has now been obtained as a pure, anhydrous substance of the formula $C_{23}H_{34}O_6$, and this also consumed an extra equivalent of alkali with stronger alkali and higher temperature. Therefore this substance, *isogitoxigenic acid*, is a lactone acid isomeric with isoperiplogenic acid and isosarmentogenic acid, but with a more stable lactone group. The retention of the secondary hydroxyl in isogitoxigenin was shown by its oxidation to the ketone *isogitoxigenon*. Strong hydrochloric acid converted isogitoxigenic acid into *anhydroisogitoxigenic acid*, by removal of the additional tertiary hydroxyl as water. The lactone group of the anhydro acid was readily decomposed by dilute alkali. Probably the proximity of the extra tertiary hydroxyl group plays a rôle in the stability of the lactone group of isogitoxigenic acid, and for similar reasons isogitoxigeninic acid exists only as the stable lactol and not as a hydroxyaldehyde. Hydroxylamine with isogitoxigeninic methyl ester gave, instead of an oxime, a substance which owed its origin to the intermediate formation of a hydroxamic acid which then lost water with the lactol hydroxyl. It is definitely concluded that gitoxigenin, like digitoxigenin, is a tetracyclic $\Delta^{8,7}$ -lactone in which a carbon atom, presumably γ to the lactone γ carbon atom, carries a tertiary hydroxyl group. In the formation of isogitoxigenin this hydroxyl functions in an oxidic union between the two carbon atoms with a disappearance of the double bond as follows :—



Attempts at further structural correlation of gitoxigenin with digitoxigenin by means of the iso-compounds will shortly be presented. P. H. P.

Standardisation of Tincture of Digitalis. F. Wokes. (*Quart. J. Pharm.*, 1929, 2, 48.)—The average potency of eight samples of English digitalis leaves was similar to that of the international standard, but the samples varied in themselves from 64 to 140 per cent. of the average. This accounts for the great variation found in the potency of the tincture. The only safeguard against this variation is a determination of their strength by biological assay. When tested by the cat

method and by the frog method, samples that are fresh give the same results, but if kept more than a month or so the frog method gives somewhat lower results, until, after a few months, the potency (as found by the frog method) has decreased to one-half to two-thirds of its original value, at which point it remains fairly constant for some years. With the cat method, however, the potency decreases much more slowly.

R. F. I.

Biochemical.

Acetone as a Control Substance for Respiration and Gas Analysis

Apparatus. T. M. Carpenter, E. L. Fox and A. F. Sereque. (*J. Biol. Chem.*, 1929, 82, 335-343.)—The use of acetone for control tests of the gasometer method, and of the Haldane portable and the Haldane-Carpenter gas analysis apparatus is described, and also the use of combinations of alcohol and acetone with the Benedict universal apparatus. Acetone has several advantages over ethyl alcohol, which was for many years the standard substance for control tests of respiration apparatus and gas analysis apparatus, but it very readily penetrates rubber. Therefore the apparatus for the supply of acetone to the burner must either have mercury-sealed joints, or else be made entirely of glass. A diagram shows the apparatus used for control tests, with acetone, of the gasometer method. It consists of a burette made on the Mariotte principle, a lamp, and a small spirometer which is raised and lowered by a wind-screen wiper. The average of sixteen periods with the gasometer method was 0.746 for the ratio of CO_2 to O_2 , and 99.9 per cent. and 100.5 per cent. for the recovery of the theoretical carbon dioxide and oxygen values. The average value of CO_2 to O_2 with the Haldane portable gas analysis apparatus was 0.751 when the changes in the composition of the air current were 2 per cent. or over. The average ratio with the Haldane-Carpenter gas analysis apparatus was 0.746. The ideal control test of a respiration apparatus would be the one that most closely imitates the biological processes, in which there is practically no constancy, *i.e.* a test in which there are quantitative and qualitative variations. The use of alcohol and acetone in various combinations was used to meet these requirements. The average ratio of CO_2 to O_2 found for the various mixtures of ethyl alcohol and acetone was 0.704 with the Benedict universal apparatus, compared with a theoretical average of 0.709. The apparatus for these experiments lacked the perfect prevention of leakage which is now known to be necessary, and with which the percentage results would probably have been comparable with those obtained with the gasometer method.

P. H. P.

Effect of Boron Deficiency on the Growth of Tobacco Plants in Aerated and Un-aerated Solutions. J. E. McMurtrey. (*J. Agric. Res.*, 1929, 38, 371-380.)—Normal tobacco plants cannot be grown to maturity in solutions containing only the usually accepted essential elements in distilled water, but if tap water is substituted growth is possible, or if boron (0.5 p.p.m.) is supplied in the distilled water solution. In boron-deficient media growth is much reduced, but still more striking is the injury to the terminal bud, which is the more pronounced in the

more vigorously growing plants, such as those growing in aerated rather than unaerated solutions. The bases of the young leaves are affected, whereas calcium deficiency in the plant affects the tips and margins. D. G. H.

Purification of Picric Acid for Creatinine Determination. S. R. Benedict. (*J. Biol. Chem.*, 1929, **82**, 1-3.)—Purification of picric acid may be satisfactorily carried out by two methods. (1) *From glacial acetic acid.*—The picric acid is dried and 100 grms. dissolved by heating in 150 c.c. of glacial acetic acid. After reaching boiling-point it is filtered hot, allowed to stand for some hours, and if the picric acid has not crystallised out, stirred vigorously or seeded with a minute crystal of pure acid. After 2 hours the liquid is filtered, and the precipitate washed by means of suction with about 35 c.c. of cold glacial acetic acid, as free of acid as possible, and dried at 80-90° C. The yield is about 60 grms. of pure acid which should read 12.5-13.5 mm. by the Folin-Doisy test. (2) *As sodium picrate.*—Six litres of water are heated to boiling in a large porcelain enamelled pail, 250 grms. of anhydrous sodium carbonate added, and when this has dissolved, 500 grms. of the moist technical picric acid are added gradually. Filtration is not usually necessary, but the clear solution is decanted from any dirt settling on the bottom. After standing, the crystallised sodium picrate is filtered off, washed with 2 litres of 10 per cent. sodium chloride solution, dried by suction as completely as possible, the suction stopped, and 500 c.c. of dilute (1:4) hydrochloric acid poured over the mixture, which is then stirred, and attached to the suction pump, 3 more portions of acid being added in succession. Finally the picric acid is washed with 2 litres of cold water, dried at 90° C., and powdered. It should read about 13.5 to 14 mm. by the Folin-Doisy test. D. G. H.

Use of Molybdic Acid as a precipitant for Blood Proteins. S. R. Benedict and E. B. Newton. (*J. Biol. Chem.*, 1929, **82**, 5-10.)—Molybdic acid may be satisfactorily used instead of tungstic acid as a blood protein precipitant, and thioneine and all non-protein blood constituents may be determined in the filtrate as with tungstic acid filtrates. Direct uric acid determinations will be too high, due to the larger amount of thioneine in such filtrates, and the modified indirect method should then be used (*J. Biol. Chem.*, 1922, **51**, 204). The molybdic acid must be of the highest purity, with practically no ammonia. Twenty-five grms. of the acid and 125 c.c. of *N* sodium hydroxide are heated to boiling, and after solution of the acid, filtered, and the residue washed with 100 c.c. of boiling water. The filtrate is cooled and diluted to 500 c.c., and the precipitating reagent is prepared by diluting 1 volume of this solution with an equal volume of 0.4 *N* sulphuric acid. The mixed solution will keep for 6 weeks. For precipitation of blood proteins 1 volume of blood is diluted with 7 volumes of water, 2 volumes of reagent added, and the mixture shaken and filtered. D. G. H.

Colorimetric Determination of the Serum Proteins. D. M. Greenberg. (*J. Biol. Chem.*, 1929, **82**, 545-550.)—Wu (*J. Biol. Chem.*, 1922, **51**, 33; *ANALYST*, 1922, **47**, 265) and Wu and Ling (*Chinese J. Physiol.*, 1927, **1**, 161) published a

method for the determination of plasma proteins based on the colour developed with Folin's phenol reagent. Folin and Ciocalteu (*J. Biol. Chem.*, 1927, **73**, 627) improved the phenol reagent by the addition of lithium sulphate. A colorimetric method is now described by the author for the determination of serum proteins based on the colour developed with Folin's phenol reagent, and on the method of Howe (*J. Biol. Chem.*, 1921, **49**, 93; *ANALYST*, 1922, **47**, 128) of salting out the globulin with sodium sulphate solution. The sodium sulphate was found to have almost no effect on the colour developed; hence the albumin can be determined directly on an aliquot part of the filtrate. The total serum protein and the albumin fraction can be determined, and the globulin found by subtraction, but it is better to determine both albumin and globulin separately. The method is rapid and relatively simple, only 0.5 c.c. of serum is needed for a determination, and results were obtained accurate to about 5 per cent. The tyrosine equivalents of the serum proteins were determined for human blood, with composite samples of serum, by parallel determinations by the colorimetric method, and by Kjeldahl's nitrogen method. The average value of the factors obtained, in terms of mgrms., of protein that give a colour equivalent to that given by 1 mgrm. of tyrosine are:—Total protein, 16.0; albumin, 16.6; globulin, 14.4.

P. H. P.

Plant Haemagglutinins with Special Reference to a Preparation from the Navy Bean. V. R. Goddard and L. B. Mendel. (*J. Biol. Chem.*, 1929, **82**, 447–463.)—A non-toxic, highly potent, soluble, haemagglutinating protein having the characteristics of an albumin has been prepared in dry form from navy beans (*Phaseolus communis*). The method of Osborne, Mendel and Harris (*Amer. J. Physiol.*, 1905, **14**, 259) for the preparation of ricin was closely followed. A quantitative, macroscopic method for the measurement of haemagglutination has been devised, and used for a study of the variables which affect the reaction. The procedure used is as follows:—Rabbit blood freshly removed from the ear vein and defibrinated was centrifuged until the serum could be removed. The corpuscles washed twice with 0.89 per cent. sodium chloride solution were suspended therein, 2.5 c.c. of packed corpuscles being suspended in a total volume of 100 c.c. of the isotonic sodium chloride solution. Aliquot parts of this suspension were used for the individual tests. As a rule, 0.5 c.c. of the corpuscle suspension was added to 0.5 c.c. (making a total volume of 1 c.c.) of 0.89 per cent. sodium chloride solution containing varying amounts of the agglutinin preparation to be tested. The reaction was carried out in chemically clean glass tubes, 75 × 8 mm., placed in a rack which would keep them at an angle of 40°, and incubated at 40–44° C., for 12 hours. Under these conditions, when agglutinin was present, the cells became firmly attached to the glass, and remained unmoved when the tube was returned to the vertical position; this adherence of cells never occurred in the absence of haemagglutinin, nor when the latter was too dilute to bring about clumping detectable upon microscopic examination. Results show that agglutinin is still active, for rabbit erythrocytes, at a dilution of 1 in 6,000,000; by analogy with immunological terminology this figure could be called its titre,

since clumping is effected in a total volume of 1 c.c. of solution containing only 0.0006 mgrm. of agglutinin by dry weight. The agglutinin gave very similar results with the erythrocytes of man, rabbit, dog and duck. The erythrocytes of the hen required 10 times as much agglutinin as rabbit erythrocytes. The indispensability of electrolytes and the inhibiting influence of certain proteins, notably those of egg albumin and the serum proteins, are demonstrated. Chemical changes in the protein which lead to denaturation or hydrolytic cleavage are shown to be accompanied by a lessened haemagglutinative potency. The mode of action, the chemical nature, and some practical aspects relating to the application of the procedures to the production of therapeutic serums are discussed. A sample of agglutinin from the bean, which had been stored for over 2 years, showed no appreciable loss in activity. The substance was obtained in the form of a nearly white powder.

P. H. P.

Determination of Sugar in Blood. I. Observations upon Benedict's Alkaline Copper Solution. M. R. Everett. (*J. Biol. Chem.*, 1929, **82**, 369–376.)—The work of Benedict (*J. Biol. Chem.*, 1925, **64**, 207; ANALYST, 1925, **50**, 414; *J. Biol. Chem.*, 1926, **68**, 759; ANALYST, 1926, **51**, 467) and Folin (*J. Biol. Chem.*, 1926, **67**, 357; ANALYST, 1926, **51**, 309; Folin and Svedberg, *J. Biol. Chem.*, 1926, **70**, 405) reveals an effect of sulphite in alkaline copper reagents which has been only partly appreciated heretofore. A careful study of the effect of sulphite upon alkaline copper reagents has now been made, and the effect is a general one. It is not entirely inactive with any copper mixture, and it always causes intense reduction by itself, if sufficient is added to a copper mixture. Without exception there is a lowering of the apparent blood sugar values, regardless of the nature of the other components of the alkaline copper solutions. Blood sugar values 10 to 20 per cent. lower than similar Folin–Wu values were always obtained with sulphite and copper reagents which contained malate, glycine salicylate, or pyridine in place of tartrate, or with reagents in which tartrate was combined with these substances, etc., and the Folin–Wu copper reagent was found to give similar low values when proper amounts of sulphite were added to it. The sensitiveness of alkaline copper mixtures to reduction by sulphite is quite variable, *e.g.* decreasing alkali concentration increases the sensitiveness. The author was studying the preparation of an ideal copper mixture, for securing low blood sugar values, containing glycine, sodium sulphite, and an inactive salt, when the new alanine, tartrate and sulphite reagent of Benedict (*J. Biol. Chem.*, 1928, **76**, 457; ANALYST, 1928, **53**, 230) was reported, and further work on the glycine reagent was unnecessary. However, it is demonstrated that Benedict's new blood sugar method does not give true blood sugar values. The apparently low values for blood sugar, given by the sulphite-containing reagents, are due partly, if not entirely, to an unequal and deceptive fading of the colours in the standard and the unknown, and not to an increased specificity for glucose. Benedict's new method has given negative values for hydrolysable blood sugar when other methods have proved the presence of appreciable amounts of such sugar. The rate of fading appears

to be different for different samples of blood filtrate. The use of 4 c.c. of Folin's acid molybdate solution seems to eliminate the unequal fading, and is suggested as a possible modification. Figures given show that the original blood sugar values are close to the Folin values, and that added glucose is apparently recovered from fermented filtrates.

P. H. P.

Dextro-rotatory Sterol of Yeast. Zymosterol. H. Penau and G. Tanret. (*Comptes rend.*, 1929, 188, 1317-1319.)—Analysis of zymosterol isolated from yeast-fat by Smedley and Maclean (*Biochem. J.*, 1928, 22, 22) indicates the formula, $C_{27}H_{42}O_2 \cdot H_2O$, corresponding with that of an oxyergosterol. This compound is markedly more soluble than ergosterol, 1 part dissolving at 18° in 18 parts of absolute alcohol, 26 of 95 per cent. alcohol, 11 of ether, or 15 of acetone; 1 grm. dissolves in 80 vols. of olive or sesame oil, whereas 325-350 vols. are required with ergosterol. The iodine value (190-201) confirms the presence of three ethylenic linkings in the molecule, which contains also two alcoholic groupings. One kilo. of fresh yeast contains from 1 to 1.5 grm. of ergosterol and 1 grm. of zymosterol.

T. H. P.

Cytological Study of Water-Soluble and Fat-Soluble Constituents of Citrus. J. Dufrenoy. (*J. Agric. Res.*, 1929, 38, 411-429.)—This work was undertaken in order to get a clearer notion of the biochemical changes which take place in the normal citrus tree and result in the production of highly attractive fruit, and to learn what undesirable biochemical phenomena are associated with various pathological conditions or blemishes. A study has therefore been made of the cells of both normal and pathological tissues; first, in the living condition, with the use of vital dyes; secondly, in the post-vital condition; and thirdly, after killing with suitable killing fluids. Twenty-one figures of histological sections are given showing stained cells of leaves and fruit. The results show that cells of green parts of citrus leaves or fruits normally contain one large vacuole, which can be stained in the living cell by the use of neutral red in 10 per cent. cane-sugar solution as a dye. Gentle excitations tend to cause the large vacuole to break into a number of smaller vacuoles. Greater shock may result in the browning of the vacuolar content and ultimately in the collapse of the cell, when the vacuolar material is thrown out of colloidal states and mixed with the cytoplasmic constituents, on which it exercises a coagulating effect. Cells of green parts of citrus contain in their cytoplasm short rod-like mitochondria and starch-forming chloroplasts. A number of conditions may result in the breaking down of the lipoprotein complex of which the normal mitochondria and plastids are made, resulting in such cytological phenomena as are naturally observed in the leaf tissues affected by puncturing of the cells, or such as may be experimentally induced in the peel of the fruit by the ethylene-gas treatment for artificial colouring. The natural colouring process of the fruit is concomitant with starch translocation from the chloroplasts in the cells of the three upper layers in the peel. As starch disappears, fat bodies develop in the chloroplasts, and the orange pigment that gives the fruit its colour goes into solution in the fat bodies inside the chloroplasts.

Artificial gas treatment gives the same result. The action of selenium salts may induce mitochondria which seem to be inactive normally, to develop red pigment.

P. H. P.

Antineuritic and Water-Soluble *B* Vitamins in Beef and Pork. R. Hoagland. (*J. Agric. Res.*, 1929, **38**, 431–446.)—As a result of feeding experiments with pigeons, the author reported (*U.S. Dept. Agric. Bull.*, 1923, **1138**, 48 pp.; *Amer. J. Physiol.*, 1924, **67**, 300) that lean pork was an excellent source of vitamin *B* (antineuritic vitamin), but that beef contained much less of this vitamin. In view of the present knowledge concerning the multiple nature of water-soluble vitamin *B* it is evident that the antineuritic value of lean pork or beef is not necessarily an indication of the amount of the vitamin *B* complex present. Therefore the relative amounts of the antineuritic and the composite water-soluble *B* vitamins in lean pork and beef have now been studied by feeding tests with pigeons and with rats, respectively. It is shown that lean pork, and fresh and smoked ham are excellent sources of the antineuritic vitamin, and compare favourably in this respect with brewers' yeast. Five per cent. of dried lean pork in a ration protected pigeons against both polyneuritis and loss in weight for 8 weeks and longer. This is equivalent to a daily intake of 1 gm. of dried pork for a pigeon weighing 400 grms. Beef contains much less of the antineuritic vitamin; from 35 to 40 per cent. of dried lean beef were required for protection, corresponding to a daily intake of from 7 to 8 grms. of dried beef for a 400 gm. pigeon. Lean pork is a good source of water-soluble *B* vitamins, but not so good as either brewers' or bakers' yeast. From 15 to 25 per cent. of dried lean pork in the diet furnished sufficient water-soluble *B* vitamins for excellent growth in rats, as compared with 5 per cent. of dried brewers' yeast. During a period of 60 days, approximately 1.6 grms. of dried lean pork or 0.5 gm. of dried brewers' yeast daily proved adequate for growth in male rats. No material difference was observed between fresh and smoked hams as sources of the water-soluble *B* vitamins. The fact that dried pork was approximately as rich in the antineuritic vitamin as dried brewers' yeast, whilst the latter was from 3 to 4 times richer in water-soluble *B* vitamins than the former, indicates that the dried brewers' yeast was correspondingly richer in the heat-stable vitamin than dried lean pork. Lean beef contained much less water-soluble *B* vitamins than lean pork; from 40 to 70 per cent. of dried, fresh beef was required for excellent growth in rats, as compared with 15 to 25 per cent. of dried lean pork or 5 per cent. of dried brewers' yeast.

P. H. P.

Chemical Detection of Vitamin C. B. Glassmann and A. Posdeew. (*Z. Unters. Lebensm.*, 1929, **17**, 191–200.)—Exhaustive experiments on the qualitative and quantitative uses of Bezssonow's phosphomolybdotungstic acid reagent for vitamin C (*ANALYST*, 1921, **46**, 411, 462; 1924, **49**, 594) have shown that the reagent is not reliable, since it reacts with tannins present in plant substances at ordinary temperatures, and with carbohydrates and other plant substances at 100° C. A close correspondence was found between the colour produced and the carbohydrate contents of a number of vitamin-containing juices, while 0.5 to 1.5

mgram. of tannic acid in 10 c.c. gives a colour which can be matched accurately against that produced with the standard solution of hydroquinone used in the experiments. It is concluded that animal experiments are at present the only reliable means of estimating vitamin C.

J. G.

Organic Analysis.

Cold Test of Fatty Oils. R. R. Matthews. (*J. Amer. Leather Chem. Assoc.*, 1929, 24, 242.)—A report has been issued on the "Cloud" and "Pour" points of neatsfoot oil by a joint committee of the American Society for Testing Materials and the American Leather Chemists' Association. The A.S.T.M. standard method D97-28 for Cloud and Pour Point of petroleum products was used by 13 analysts on two neatsfoot oils, one of a low and one of a high cold-test. The report states that the Pour Points agreed closely. The table given shows that for the low cold test oil eleven members returned it as 20° F., one as 15° F., and one as 10° F. For the high cold test oil ten members reported the Pour Point as 25° F., and the other three as 15° F., 20° F. and 30° F. Two further samples of oil were sent out for the purpose of comparing the test at 2° intervals with that at 5° intervals. Complete concordance was not obtained in either case, and no advantage is gained by taking readings at 2° intervals.

The test for Cloud Point was not reliable, and it was decided to do nothing further on it so far as fatty oils are concerned.

R. F. I.

Action of Bromine on Insect Oils. J. Timon-David. (*Comptes. rend.*, 1929, 17, 1122-1124.)—The iodine values of certain insect oils, particularly of the Lepidoptera, are high. The iodine values (Wijs) of the following caterpillar oils were:—*Vanessa urticae* L., 159.7; *Pieris brassicae* L., 149.9; *Saturnia Pernyi* Guer., 140.4; *Arctia caja* L., 133.3; *Malacosoma franconica* Esp., 138.0; and, of the Chrysomelids of the Coleoptera, the iodine value of the oil from the larvae of *Colaspidema atra* Ol. was 113.4; that of the imago of *Leptinotarsa decemlineata*, Say., 108.6, and of *Galerucella luteola*, Mull. 118.2. The action of bromine showed that the oils may be classified as: (1) Those giving high hexabromide values (*Saturnia pernyi*, Guer., *Pieris brassicae* L.); lower hexabromide values (*Colaspidema atra* Oliv., *Leptinotarsa decemlineata* Say., *Thaumetopoea pityocampa*, Sch.); and no hexabromide values (*Ergastes faber* I., *Pyrausta nubilitalis*, Hubn.). The differences are probably largely due to methods of feeding.

D. G. H.

Determination of Hygroscopic Moisture in Coals. H. Löffler. (*Chem. Ztg.*, 1929, 42, 411.)—The method recommended, especially suitable for brown coals, is a modification of that of Abderhalden and Blacher in which the coal is dried in a vacuum at 60° to 70°. The modification consists in a more regular application of the heat. One or two grms. of the coal are placed in a weighing-tube inserted horizontally in the neck of a wider tube, through which the vapour of a liquid of the required boiling point freely passes. The liquid is contained in an electrically heated conical flask, loss being avoided by a globe condenser. The

end of the weighing-tube is connected with one end of a retort of special shape, the narrow end of which leads to the vacuum pump. In the body of the retort is placed granulated calcium chloride. During the test the pressure is reduced to 10 mm., and the heating continued for one hour at most. The weighing-tube containing the dried coal is then removed, the stopper inserted, the whole cooled in a desiccator and the loss of weight determined. Agreement in duplicates is within 0.1 per cent. The apparatus is obtainable from Messrs. Woytacek, Starhembergasse, Vienna IV.

R. F. I.

Determination of Nitrogen by the Kjeldahl Method, applied to the Analysis of Colouring Matters and Intermediates. P. Sisley and M. David. (*Bull. Soc. Chim.*, 1929, 45, 312-324.)—The various modifications suggested to render the Kjeldahl method applicable to compounds in which the nitrogen present is united either to another nitrogen or to an oxygen atom, are discussed. The low results obtained with nitrobenzene, *p*-nitrotoluene, etc., are due to loss of the substance by volatilisation; preliminary sulphonation helps in these cases, but is not of universal application.

The following procedure yields accurate results for the nitrogen content of a large number of nitro-, nitroso-, azoxy-, and azo- compounds. From 0.5 to 1 grm. of the substance, according to its nitrogen content, is heated in a 250 c.c. pyrex flask with 10 c.c. of pure alcohol and 5 c.c. of water. From 2 to 4 grms. of sodium hydrosulphite are then added in 1 grm. quantities, the liquid being heated to boiling under a reflux condenser after each addition. With substances which are readily soluble and reducible, it is not necessary to heat to boiling, decolorisation being rapid; substances sparingly soluble in water must be very finely powdered. After completion of the reduction, which requires at most 10-15 minutes, the flask is allowed to cool, 10 c.c. of sulphuric acid (66° Bé.) being then added. The liquid is heated gently, with the neck of the flask inclined, so that the bulk of the alcohol is expelled. When the liquid begins to froth, 0.5 grm. of copper sulphate, 6-8 grms. (10 grms. less the weight of hydrosulphite used), and 12 c.c. of sulphuric acid are added. The heating is continued, at first gently and afterwards more strongly, for 20 to 30 minutes, when the liquid should have a pure blue colour. The solution is diluted to 300 c.c. in a 700 c.c. Erlenmeyer flask, and is then treated with excess (100 c.c.) of sodium hydroxide solution (36° Bé.), 5 c.c. of freshly prepared 20 per cent. sodium sulphide solution, and a little granulated zinc. The distillation is carried out in the Wagner apparatus, the boiling being continued for 45 minutes. The best indicator is methyl red.

T. H. P.

Inorganic Analysis.

Separation of Beryllium from Aluminium, Iron, and Copper by *o*-Hydroxyquinoline. M. Niessner. (*Z. anal. Chem.*, 1929, 76, 135-145.)—As beryllium does not form an insoluble hydroxyquinolate, the reagent permits of the following rapid and accurate separations:—*From aluminium.*—The neutral or feebly acid solution (200 to 300 c.c.) is heated to 70° C., stirred vigorously, and an

excess of precipitant (a mixture of strong ammonium acetate and 2 per cent. alcoholic hydroxyquinoline solutions) is added. The precipitate is left to settle on a water-bath at 70° C., collected on a porous glass crucible, and washed with hot water until the washings are colourless. It is weighed after drying to constant weight at 110° C. The beryllium in the filtrate is precipitated by boiling with ammonia. *From iron.*—The operation is like the preceding, 2 grms. of tartaric acid having been added to the solution. *From copper.*—The copper is precipitated according to Berg's directions (ANALYST, 1927, 52, 302) from acetate solution, and the beryllium in the filtrate is precipitated with ammonia. (Cf. Kolthoff and Sandell, ANALYST, 1928, 53, 508.)

W. R. S.

Uranyl Zinc Acetate as Reagent for the Quantitative Determination of Sodium. I. M. Kolthoff. (*Chem. Weekblad*, 1929, 26, 294–298.)—The investigations of the author and others on this reagent (Blanchetière, ANALYST, 1923, 48, 456; Kolthoff, *id.*, 1927, 52, 304; 1928, 53, 456) are summarised. Sodium (0.002 to 0.04 per cent.) may be detected in salts of zinc, iron, potassium, copper, lead, bismuth, mercury, or cadmium. Arsenates, ferrocyanides and oxalates interfere, phosphates should be removed by magnesia mixture, and sulphates as barium sulphate. Ammonium, zinc and magnesium salts do not interfere. For quantitative work an accuracy of +0.5 to –0.2 per cent. is normally obtainable if the alcohol used for washing purposes is previously saturated with the triple salt, which is soluble in water, insoluble in the reagent or in 95 per cent. alcohol, and slightly soluble in absolute alcohol. Sodium in potassium chloride is determined by the addition to 1 gm. of sample in 5 c.c. of water of a warm solution of 2 grms. of ammonium perchlorate in 3 c.c. of water and 25 c.c. of 95 per cent. alcohol. The cooled mixture is then filtered, washed 5 times with 2 c.c. of 95 per cent. alcohol, the filtrate evaporated, the residue dissolved in 1 c.c. of water, and the sodium precipitated with 10 c.c. of reagent. An accuracy of 1 per cent. is obtainable for potassium salts containing 0.1 per cent. of sodium. Sodium in lithium salts is determined, after removal of the lithium, by Palkins' method (*id.*, 1917, 42, 54), or as carbonate or fluoride. A solution of 0.2 gm. of salt in 10 c.c. of water is allowed to stand for 20 hours with 5 c.c. of a 10 per cent. ammoniacal solution of ammonium fluoride and 10 c.c. of 96 per cent. alcohol, and the lithium fluoride filtered off and washed with 50 per cent. alcohol containing a little ammonium fluoride. The filtrate is evaporated with 8 c.c. of 6 N hydrochloric acid, and the sodium determined in the residue. The method, which may be combined with the determination of lithium, may be used for 0.01 per cent. of sodium in 0.5 gm. of lithium chloride.

J. G.

Simultaneous Determination of Orthophosphate and Pyrophosphate.

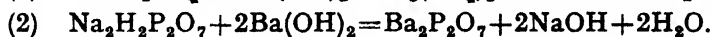
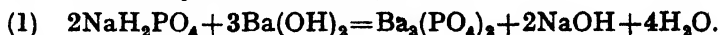
- (a) R. Dworzak and W. Reich-Rohrwig. (*Z. anal. Chem.*, 1929, 77, 14–37.)
(b) W. Stollenwerk and A. Bäurle. (*Id.*, 81–111.)—(a) The gravimetric method of Berthelot and André was modified as follows: The solution of the phosphates (total phosphorus about 0.2 gm.) is added to a mixture of 100 c.c. of acid magnesia mixture ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, 55 grms.; NH_4Cl , 105 grms. per litre, faintly

acidified with hydrochloric acid against methyl red), and 20 c.c. each of ammonium chloride and acetate solutions, both saturated in the cold; the precipitate is dissolved by addition of 40 c.c. of 2 *N* acetic acid. The liquid (200 to 300 c.c.) is heated on the water-bath for 4 to 5 hours in the covered beaker, after which the magnesium pyrophosphate is collected and washed with hot water containing ammonium chloride and acetate, and acetic acid. Concentration of the filtrate on the water-bath yields another 0.5 to 3 per cent. of the pyrophosphate present, which is treated like the bulk. The filtrate will now remain clear, even on more protracted heating; the orthophosphate contained therein may be determined as usual. The pyrophosphate precipitates are dissolved off the filters in warm dilute nitric acid, and the solution boiled for an hour; its orthophosphate content is then determined. The method is satisfactory except when the relative amount of pyrophosphate is small; in this case the addition of the 2 *N* acetic acid is reduced to 1 to 5 c.c., and the solution evaporated on the water-bath to small bulk.—A volumetric method was elaborated: it answers well except for mixtures containing very much pyrophosphate. It is based on the property of metallic (*e.g.* stannic) pyrophosphate precipitates of re-dissolving, with the formation of soluble complexes, so long as the soluble pyrophosphate is in excess; when an excess of metallic salt is added to such a solution, a cloudiness appears as soon as a definite ratio of base to acid is exceeded. A solution of uranium acetate (20 grms. per litre) is used, and its uranium content determined gravimetrically. Twenty-five grms. of the salt to be tested are dissolved in 500 c.c. of water, and 25 c.c. portions measured out. A preliminary test is made, in which the solution diluted to 150 c.c. is titrated, with constant stirring and dropwise addition of the uranium solution, to permanent cloudiness. For the final determination, the aliquot portions are treated with a quantity of *N* ammonia depending on the ascertained volume of uranium solution: 0.1 for 10, 0.5 for 20, 1.5 for 30, 2.5 for 40, and 4 c.c. of ammonia for 50 of uranium solution. The ten portions are then titrated with the uranium solution, the first portion being given 5 to 7 c.c. less than was ascertained for the preliminary test, and each succeeding portion one c.c. more than its predecessor. After an interval of at least 6 hours, the assays are inspected, some being clear, the others cloudy. The volume of uranium solution required lies between those of the last clear and the first cloudy test; the intermediate reading is estimated according to the depth of the cloudiness. The calculation is based on the ratio $U=2P_2O_5$, the formula of the complex probably being $Na_6[UO_2(P_2O_7)_2]$, whence $Na_4P_2O_7=2.234U$.

(b) The analytical application of the pyrophosphates of silver, copper, the alkaline earths, beryllium, aluminium, and lead was investigated; they proved unsuitable for quantitative purposes, with the exception of the alkaline-earth compounds. The process worked out is an indirect one, the phosphates being precipitated by baryta of known strength, with subsequent gravimetric or volumetric determination of the excess of precipitant. The precipitates are always the fully saturated salts $Ba_3(PO_4)_2$ and $Ba_2P_2O_7$. For the gravimetric determination, 1 gram. of the salt is dissolved in 200 c.c. of distilled water; an aliquot volume is diluted to 50 c.c. in a 200 c.c. flask, boiled, treated with an excess of

0.025 *N* barium hydroxide, cooled to room temperature after insertion of a soda-lime tube, and made up to bulk with carbon dioxide-free water. After settling, 100 c.c. are filtered through a dry Gooch crucible, and the excess of baryta in the filtrate determined as sulphate. In another portion the total P_2O_5 is determined as $MgNH_4PO_4$ after 15 minutes' boiling with dilute nitric acid. Let $B = BaO$ combined with P_2O_5 ; $P = \text{total } P_2O_5$; $X = \text{ortho-}P_2O_5$; $(P - X) = \text{pyro-}P_2O_5$; then $\frac{460.11X}{142} + \frac{306.74}{142} (P - X) = B$, whence $X = \frac{142B - 306.74P}{153.37}$. For the

volumetric determination, the salts must be converted into NaH_2PO_4 and $Na_2H_2P_2O_7$ by neutralisation with acid against methyl orange; a measured excess of 0.1 *N* barium hydroxide is then added:



The excess of baryta is ascertained in one-half of the filtrate, which is run into an excess of standard acid to prevent precipitation of carbonate; the excess acid is titrated with standard alkali (1 c.c. 0.1 *N* alkali = 0.00355 grm. ortho- P_2O_5 and 0.0071 grm. pyro- P_2O_5). Let $x = \text{c.c. } 0.1 \text{ } N \text{ alkali combined to orthophosphate}$, $a = \text{c.c. total alkali}$, and $P = \text{total } P_2O_5$, then $P = 0.00355x + (a - x) 0.0071$.

W. R. S.

Colour Indicators for Permanganate Titrations. (a) **Determination of Ferrocyanide.** J. Knop. (*Z. anal. Chem.*, 1929, 77, 111-125.) (b) **Determination of Iron.** J. Knop and O. Kubelkova. (*Id.*, 125-130.)—(a) The two following triphenylmethane dyes are suitable as indicators in permanganate (not dichromate) titrations: (1) "*Erioglaucin A*" and (2) "*Eriogrün B*," made by *Anilinfarben- und Extraktfabriken vorm. J. R. Geigy*, Basle. They are used in 0.1 per cent. aqueous solution. One c.c. of (1) (blue), added to 200 to 400 c.c. of an acidified solution, produces a green colour, giving a grey transition tint with 0.1 c.c. of 0.01 *N* permanganate; a further 0.2 c.c. changes the colour to red. Two c.c. of (2) (blue-green) under the same conditions produces a yellow liquid giving a full orange-yellow tint with 0.1 c.c. of the permanganate solution. The colour changes are reversible, and the coloration is more intense than that of permanganate. For the titration of ferrocyanide, less than 1 grm. of salt is dissolved in 400 c.c. of water and 20 c.c. of 8 *N*-sulphuric acid. The above quantities of either indicator are added, and the solution titrated with 0.05 *N* permanganate. The colour changes in presence of ferricyanide are: Yellowish-green to orange-brown for (1), full yellow to orange-yellow for (2). Artificial light does not vitiate the result, and the end-point is more easily observed. (b) In the permanganate titration for iron, the transition in the acid sulphate solution is from grass-green, over grey to red for (1), from yellow to orange for (2). The indicators proved specially suitable in micro-work.

W. R. S.

Determination of the Purity of Potassium and Sodium Ferrocyanides by Titration with Zinc Sulphate Solution. *Farbsalz-Gesellschaft, Berlin.* (*Chem. Ztg.*, 1929, 53, 399.)—Discrepant results having been obtained owing to

the use of different methods of analysis, most of the firms interested in ferrocyanides now precipitate with zinc sulphate, the product formed containing two $\text{Fe}(\text{CN})_6$ groups per three atoms of zinc. The titre of the zinc sulphate solution, containing 28.755 grms. of the pure salt per litre, is determined by means of a solution containing 10 grms. of potassium ferrocyanide in 500 c.c. Fifty c.c. of the latter, diluted with 100 c.c. of water, and mixed with 10 c.c. of 0.1 *N* iron-free sulphuric acid, are titrated with the zinc sulphate solution at 15–20° C. To determine the end of the titration, 2 or 3 drops of the liquid are transferred by a thin glass rod to the same place on a strip of ash- and iron-free filter-paper and, after 20 or 30 seconds, when the liquid has spread, a similar amount of aqueous 15 per cent. pure ferric ammonium alum is placed close by on the paper: no blue colour should appear at the contact point of the liquids within 2 or 3 minutes.

In carrying out the drop test, small depressions should be made in the filter-paper with a glass rod and the drops should be placed in depressions 1–1½ cm. apart. The drops should flow together slowly, so that the precipitated zinc ferrocyanide does not come into contact with the ferric ammonium sulphate. The preliminary test should be followed by a more exact one.

The procedure is similar in determining the purity of a commercial ferrocyanide. The titre of the zinc sulphate solution must be determined with either sodium or potassium ferrocyanide, according to whether the sodium or potassium salt is to be analysed, since different results are obtained with the two salts. Moisture in ferrocyanides is determined by drying to constant weight at 125° C., the excess (over the water of crystallisation) corresponding with the proportion of pure salt present being extraneous moisture. (*Cf.* ANALYST, 1929, 38.)

T. H. P.

Reviews.

ESSENTIALS OF QUALITATIVE CHEMICAL ANALYSIS. By J. C. WARE, Sc.M., Ph.D.
Pp. xii + 351, with 27 illustrations and 6 coloured plates. London:
Chapman & Hall, Ltd. 1928. Price 17s. 6d. net.

This volume is intended for the use of students who propose to adopt the profession of analytical chemistry, and provides a thorough grounding in the theoretical principles of analysis and their application in practical work. For those merely taking chemistry as a subsidiary subject in a degree course the book is too detailed in the earlier portions, since before taking up practical work the beginner is expected to possess a reliable knowledge of ionisation, equilibria, solubility products, partition coefficients, etc., for which, unfortunately, the time of this class of student is too limited.

The book is divided into five parts, the first of which deals with the various fundamental factors involved in solution and precipitation. Parts II and III give the reactions and separations of some two dozen common metallic radicals and of a similar number of acidic radicals in simple solution. Part IV provides complete schemes and separation tables for the analysis of complex mixtures, both solid and in solution, based upon the earlier work, and the text is brought to a close by suggestions for the arrangement of courses, the preparation of reagents and other solutions, the management and equipment of a general academic laboratory, and various tables of service in analytical work.

The illustrations comprise, in addition to 11 figures of apparatus, some 15 half-tone reproductions of photographs taken in various American industrial laboratories, together with one of historic interest, depicting Liebig's famous laboratory as it appeared in 1846. The idea of these is, no doubt, to stimulate the interest of the student, but whether this is achieved or not, such pictures add to the value of the work. The plates depict the colours obtained in various reactions, flame tests and borax beads, and, with one or two exceptions, give an accurate rendering of the actual tints observed in practice. It is unfortunate that the references to these plates in the text are not indicated by page numbers, although these occur in the index.

The text is legible and lucid, although occasional traces of American grammar and expression are evident, but these do not introduce any ambiguity. The preface provides sound and useful advice for the student, and contains a few somewhat facetious sentences on the names given to the colours of precipitates, etc. Notwithstanding this, in the text such descriptions as "seal brown," "shell pink," and "flesh colour" occur, the last being given as the hue of manganese sulphide on p. 109, whereas the same precipitate is stated to be "pink" on p. 165.

This volume is remarkably free from typographical and other errors, the few encountered being of minor importance, but it is probable that English demonstrators will disagree with the advice given on p. 116: "it is not necessary to obtain perfect tests (for a radical) by all methods. Obtain one good test and be satisfied with that."

The analytical schemes, whilst in general following the usual groupings, are excellent, and include some novel modifications which facilitate precipitation and separation and avoid the usual students' wastage of hydrogen sulphide.

An admirable feature of this volume is the series of questions inserted at the end of each chapter and also introduced throughout the text. These are so framed as to test the student's knowledge of the reactions he is performing and to ensure a complete understanding of the basic principles of analysis.

The text-book is, as a whole, an admirable production, is provided with an adequate and accurate index, and is by far the best and most educative work on elementary qualitative analysis that the reviewer has yet seen. At the price charged the volume is exceedingly good value, and well deserves the attention of all interested in the teaching of analytical chemistry.

T. J. WARD.

THE PROBLEM OF FERMENTATION: THE FACTS AND HYPOTHESES. By M. SCHOEN, with an introduction by Professor A. FERNBACH. Translated from the French by H. LLOYD HIND, B.Sc., F.I.C., and revised and enlarged by the author. Pp. xii + 211. London: Chapman & Hall. 1928. Price 21s. net.

The appearance of a work on this important subject is a welcome addition to scientific literature, and the author—so long associated with Professor A. Fernbach at the Pasteur Institute in Paris—is well qualified for the task of writing it. It may, indeed, be said that he has produced a book that will be appreciated by all who are interested in the fundamental branch of biochemistry with which it deals.

From the earliest times the study of fermentation phenomena has attracted the attention of those on whose work modern biochemical science is founded. The chief interest has, for obvious reasons, been centred in the change brought about by the action of yeast on sugar. But dating from the classical work of Pasteur to the present time, it has been recognised that alcoholic fermentation has a significance far beyond the production of beer and wine.

Alcoholic fermentation has, as Professor Fernbach remarks in the introduction to the book before us, "become the prototype of chemical actions brought about by micro-organisms," and we may add that together with its congeners it has been shown to occur in anaerobic respiratory processes in the higher organisms. A book on so comprehensive a subject should therefore command a wide circulation.

Pasteur's theory that fermentation is life without air has been frequently attacked, because that eminent *savant* could not show that in presence of air fermentation of sugar by yeast is completely arrested. As Dr. Schoen points out, Pasteur proved that the quantity of alcohol formed by unit weight of yeast in unit time is less in presence than in absence of air. But he recognised also that multiplication of cells can only occur continuously in presence of oxygen, observations that have been made use of in the manufacture of fermented beverages, as well as in that of yeast itself. This matter is discussed in the opening chapter of Dr. Schoen's book, in which the recent observations of Meyerhof are cited as completely proving Pasteur's theory.

The book is divided into fourteen chapters in which a connected account is given of the chemistry of fermentation, which may now be regarded as one of the forms of intramolecular or anaërobic respiration. The latest views on the nature of the intermediate products of alcoholic fermentation are discussed, and the conclusion arrived at by the author is that pyruvic acid is an indispensable link in the chain of reactions leading to the conversion of sugar into alcohol and carbon dioxide. He does not, however, deny that this acid may be formed through the intermediary of methyl-glyoxal, although this latter has never been isolated from fermentation products. A clear and concise account is given of the significance of the hexose phosphates (discovered independently by Harden and Young and by Iwanoff in 1906), in alcoholic fermentation, muscle contraction (Embden) and ossification (Robison). We presume that the work of Robison on the existence of a

monophosphoric ester of trehalose, and that of Morgan and Robison on the constitution of hexosediphosphoric acid, appeared too late for an account to be included in the text.

In dealing with the hexoses, the author speaks of the epimeric α - and β - forms as tautomeric forms. As regards the structure of the hexoses, the normal forms are stated, quite correctly, on the evidence of Charlton, Haworth and Peat (1926), to possess an amylenoxide ring, but no mention is made of the observation of the last-mentioned authors that the γ -sugars possess a butylene oxide ring. Indeed, Irvine's work is cited, without qualification, that γ -glucose possesses a propylene oxide ring, and that γ -fructose possesses an amylenoxide ring. Structural considerations are of the utmost importance to the subject matter of the book, for recent work has indicated that the γ -sugars and the normal sugars each play their own specific rôle in metabolism.

The chapter on hydrogen and the phenomena of fermentation, which appears only in the English edition, is dealt with historically and constitutes one of the most valuable portions of the book. In an earlier chapter the author had rightly claimed that recent facts—more especially those put forward by Meyerhof—apparently far removed from fermentation phenomena, had accorded to Pasteur's conception of fermentation the demonstration he desired. The idea that active hydrogen, and not active oxygen, is the initiator in oxidation-reduction changes was first shown to be possible by Pasteur's discovery of anaërobic organisms. This idea of active hydrogen as the initiator of respiratory changes has been developed by Wieland and by Thunberg, who believe it to apply generally. Warburg, on the other hand, favours the view that active oxygen in presence of iron and other metals is the initiator in changes of the kind under discussion. The arguments *pro* and *con* are set forth clearly in the book. May it not be, however, that both views are correct according to circumstances? The autoxidisable substance, glutathione, discovered by Hopkins, is present in tissues, for the most part in the reduced form; but both the oxidised and the reduced forms are catalysed by iron and other metals, as shown by Harrison.

The author does well in this chapter to point to the observations of Quastel and of Kostytschew, who throw doubt on the existence of so many specific enzymes which it has become the fashion of workers—especially in Germany—to postulate. For every supposed intermediate product between sugar and alcohol—even although these may be present in mere traces—the existence of a specific enzyme has been assumed by some investigators. Pasteur likened fermentation to an explosion, and if the change of sugar into alcohol and carbon dioxide consists of a series of explosions—and this is coming very near to Liebig's original hypothesis—it appears to the reviewer that it is unnecessary to assume the existence of so many and various intermediate products. The fact that there are products besides alcohol and carbon dioxide and that the quantity of these may be varied according to conditions, simply shows that the explosive wave can proceed in more than one direction.

Taking a general survey of this work, we can unhesitatingly recommend it to chemists who desire to obtain in a concise form the latest facts and theories concerning fermentation phenomena. The sequence is such that the book may be read from beginning to end and the arguments followed, so well are they connected. To the translator, Mr. H. Lloyd Hind, must be accorded praise for the excellent manner in which he has rendered the original French text into English. A useful bibliography and a subject-matter index are appended to the book.

ARTHUR R. LING.

DAIRY BACTERIOLOGY. By BERNARD W. HAMMER. Pp. 473 + xii. New York: John Wiley & Sons, Inc.; London: Chapman & Hall. Price 25s.

This book, which is based on the author's course in Dairy Bacteriology at Iowa State College, has for its main theme the application of bacteriological investigation to the problems of dairy practice. Such matters as the elements of laboratory technique or the detailed construction of dairy plant are not dealt with, but the numerous references to the research literature of the subject and the wealth of experienced advice contained therein make this work one which the student will take with him into practice; to the British or European worker it will, among other things, afford a key to the vast volume of investigation which appears in the bulletins of the splendidly equipped agricultural research institutions of the United States.

In Chapter I the relative advantages and disadvantages of the various methods of making routine bacterial counts in milk are discussed at length; in judging the American municipal standards for milk counts, legalised or proposed, which are given here, it may be well to remember that the standard meat extract, peptone and salt agar at 37° C., as laid down by the American Public Health Association, is by no means an ideal medium for the growth of the organisms which develop in milk under usual conditions; under the heading "Research Counts" evidence is given as to the increased counts obtained on the addition of sugars to such a medium, while in Chapter VIII, under "Pin-point colonies from Pasteurised Milk," one notes with interest that "the small amount of lactose carried over in a 1/100 c.c. dilution of milk was a factor enabling certain organisms to grow on the plates." In Chapter XVI, on the tests for the quality of milk, it is seen that the methylene blue reductase test has been gradually gaining favour in America. The classification of milk according to reduction times, as originally worked out by Barthel and Orla Jensen, is given here, but the directions as to the concentration of the dye to be used are rather vague; although some subsidiary investigations on the subject are noted, no reference is made to the pioneer work of the investigators just mentioned.

Chapter II, on milk fermentations, contains some detailed descriptions of the biological and cultural features of common milk organisms, but lacks a general survey of the relationships of the various groups of lactic acid organisms to one another. Although the necessity of repeating work of this nature under local

conditions is fully recognised, yet it must be remarked that this chapter is singularly lacking in references to modern European work. There is some very useful general advice on the investigation of milk defects. In Chapters III and IV we find a valuable survey of numerous practical trials by American workers, in which every conceivable source of milk infection has been critically investigated. The conclusions reached as to the most effective means of reducing milk contamination (not always the most obvious at first sight) will be of interest to all concerned with the improvement of milk supplies. Chapter V, dealing with bacterial growth in milk at various temperatures, treats almost exclusively of the work of American investigators; some European references would have rendered the account more complete, as, for example, in the case of milk held at temperatures above 37° C. Chapter VI treats of body cells in milk, and Chapter VII, which extends over 84 pages, gives a very full account of the most important American, British and European investigations of the spread of diseases through milk. Chapter VIII, on the preservation of milk, deals efficiently with the bacteriology of pasteurisation, in which field American workers have done such valuable pioneer work.

The sections and chapters dealing with the bacteriology of milk powder, condensed milk, ice cream, butter and cheese, contain much information that will be of use to those interested in these products. Chapter XII deals in a very practical way with the preparation of butter cultures, and is particularly valuable, as it contains an account of Professor Hammer's important researches on the associated aroma bacteria. In Chapter XIV the manufacture of butter is naturally considered with regard to American practice, but there is much that will be of interest to those concerned with butter-making in other countries, especially the information dealing with the flavour and keeping power of butter, as they are affected by the use of ripened or unripened cream, and the addition of culture to unripened cream immediately before churning.

This work will undoubtedly take its place as a standard text-book of Dairy Bacteriology, and the author is to be warmly congratulated on its production.

PAUL ARUP.

ORGANIC SYNTHESSES: AN ANNUAL PUBLICATION OF SATISFACTORY METHODS FOR THE PREPARATION OF ORGANIC CHEMICALS. Vol. VIII, pp. 141+vii, and Vol. IX, pp. 108+v. Editors in chief: R. Adams and J. B. Conant, New York: John Wiley & Sons, Inc.; London: Chapman & Hall, Ltd. Price, Vol. VIII, 10s. net; Vol. IX, 8s. 6d. net.

Workers in the field of organic chemistry are often delayed by the lack of some particular substance. On looking up the literature it is found that the methods given are in some way unsatisfactory, and, in consequence, much time is wasted in the efforts to evolve a suitable procedure. It was in order to minimise the recurrence of this state of affairs that a band of American chemists determined to publish annually a list of organic preparations which "will work." Thus "Organic Syntheses" sprang into being, and nine useful volumes have, so far, been published.

The essence of the whole scheme is that the editors have taken steps to check each preparation submitted to them, and where they have failed to repeat one, they carefully refrain from publishing it.

Each volume contains details of a number of preparations arranged as follows: First comes an equation or scheme representing the reactions involved; second, a detailed procedure; third, a set of notes giving additional information concerning various points in the method, condition of reagents, etc.; fourth, a summary of methods that have been used to prepare the substance in question; and finally, a list of references.

The volumes under review are up to the standard of clearness and conciseness set by the previous members of the series. Every effort has been made to make them as useful as possible, and, in some cases, where the question of the availability of raw material may cause difficulty to workers in various countries, alternative methods are given. Thus in Vol. VIII alternative preparations are given for β -chloropropionic acid and for trimethyl acetic acid.

The preparations given are, for the most part, those of substances which might be needed as the starting point for some line of research. Thus in Vol. IX details are given for cyanoacetamide, iodobenzene and *ac*-tetrahydro- β -naphthylamine, and in Vol. VIII details are given for benzoylformic and cyanoacetic esters. It is therefore obvious that any one requiring a substance not otherwise obtainable will do well to consult these volumes. The reviewer has rather painful memories of trying to obtain a satisfactory yield of *o*-bromotoluene and now finds in Vol. IX, p. 22, not only a simple method of preparation for this substance, but also the cause of the comparative failures which hampered the progress of research. Teachers, too, will find many a preparation which can be given to keen students, and the latter will find many practical details worthy of attention.

Excellent and characteristically American Indexes are provided. Vol. VIII contains an author index for all volumes from I to VIII, and also a subject index of the same range. Volume IX contains only a subject-index for volumes I to IX.

The volumes are of sterling value. All engaged in manufacture or research will, when in need of a substance, do well to consult these volumes before starting on their work. On the whole, the books are very useful additions to the literature of practical organic chemistry and deserve a place on the book shelves of all chemists.

HAROLD TOMS.

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

The Differential Halogen Absorptions of Oils and Fats.

By J. W. GROXFORD.

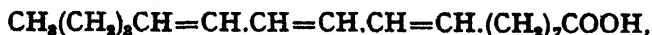
(Work done under the Analytical Investigation Scheme.)

(Read at the Meeting, May 1st, 1929.)

It was considered that an investigation into the differential halogen absorptions of some of the more common oils and fats would be of theoretical interest, and possibly of some analytical value, in helping to determine the position of the unsaturated linkings in the various fatty acid molecules contained therein.

EXPERIMENTAL.—The iodine, bromine and chlorine values of a series of oils and fats, etc., were determined, the usual Wijs method being used for the iodine values, whilst the bromine values were determined volumetrically by using an approximately *N*/5 solution of pure bromine in glacial acetic acid, with subsequent addition of 10 per cent. potassium iodide solution, and titration with a standard solution of sodium thiosulphate (as in the Wijs iodine method), and gravimetrically by the method of Toms (*ANALYST*, 1928, 53, 69). The chlorine values were determined by a modification of the gravimetric bromine vapour method. Attempts were also made to effect direct combination with iodine, by using iodine vapour, but, owing to the condensation of the iodine on the oil on the one hand, and the removal of any excess being prevented by the instability of the iodine compound to heat, and even in the vacuum desiccator, on the other, these attempts were unsuccessful. The pure unsaturated organic acids used only absorbed traces of iodine after some hours' exposure.

TUNG OIL AND ELAEOSTEARIC ACID.—Toms (*loc. cit.*) showed that tung oil gives results by his bromine method in a short time (although the figures obtained are much higher, which was accounted for in his paper), whilst days are required by the Wijs method. Elaeostearic acid



was prepared from tung oil by the method of Böesenken (*cf. ANALYST*, 1928, 53, 54), but the β -modification (m.p. 71° C.) was obtained, probably owing to exposure to light during recrystallisation. This acid behaved similarly to tung oil, giving rapid absorptions with bromine and chlorine vapours, and being very slow with Wijs method.

Substance.	Iodine value.		Bromine solution.			Bromine vapour.		Chlorine vapour.		
	Theory.	Wijs.	Br. value. Theory.	Br. value.	Iodine value. Calcd.	Br. value.	Iodine value. Calcd.	Chlorine value. Theory.	Cl. value. Observed.	Iodine value. Calcd.
Tung oil ..	—	4 hrs. 152.3	—	4 hrs. 95.5	151.6	40 mins. 140.3	222.7	—	80 mins. 61.8	221.1
β -Elaeostearic acid (m.pt. 71° C.)	181.4	18 hrs. 177.5	114.2	18 hrs. 106.5	169.0	2 hrs. 165.9	263.4	50.7	2 hrs. 74.1	265.1

COMPARATIVE RESULTS WITH UNOXIDISED OILS.—A series of ordinary unoxidised oils gave fairly concordant results with three of the four methods, but the chlorine vapour method gave in some cases high results, owing to substitution by the more active element. This substitution apparently reaches a maximum. In the case of coconut oil, larger films were used in the vapour absorptions, owing to the large proportion of saturated glycerides present.

Oil.	Iodine value. Wijs.	Br. solution.	Iodine value. Calcd.	Br. vapour.	Iodine value. Calcd.	Chlorine value.	Iodine value. Calcd.
Linseed	4 hrs. 173.6	4 hrs. 107.6	170.8	30 mins. 109.7	174.1	1 hr. 48.8	174.6
Rubber seed ..	4 hrs. 140.8	4 hrs. 84.2	133.7	40 mins. 88.7	140.9	1 hr. 39.6	141.7
Soya bean	4 hrs. 132.5	4 hrs. 79.3	126.0	40 mins. 84.2	133.6	30 mins. 36.6 1 hr. 40.8 7 hrs. 49.35 maximum	131.0 145.9 176.5
Coconut	1 hr. 7.8	1 hr. 4.8	7.6	30 mins. 5.0	7.9	40 mins. 2.3	8.2
Maize (?)	2 hrs. 101.3	2 hrs. 63.2	100.3	30 mins. 63.0	100.0	15 mins. 29.0	103.7
Olive	2 hrs. 85.0	2 hrs. 52.1	82.75	30 mins. 54.5	85.3	15 mins. 24.5 30 mins. 29.5 1 hr. 30.0 7 hrs. 49.5 maximum	87.6 105.6 107.3 177.0
Almond	2 hrs. 100.7	2 hrs. 59.35	94.2	30 mins. 64.0	101.6	30 mins. 29.3	104.8
Whale	3 hrs. 114.5	3 hrs. 70.05	111.2	40 mins. 73.4	116.5	45 mins. 32.9	117.7
Cod liver	4 hrs. 170.1	4 hrs. 101.0	160.3	1 hr. 108.6	172.4	1 hr. 45.8 1½ hrs. 52.5 2 hrs. 53.3 maximum	163.8 187.8 190.7

In the above and subsequent tables where a maximum is stated, no further absorption occurred on additional exposure for 1 hour.

CASTOR OILS AND RICINOLEIC ACID.—Ricinoleic acid, $C_{17}H_{33}(OH)COOH$, or $CH_3.(CH_2)_5.CH(OH).CH_2.C_{10}H_7.CO_2H$, was prepared from pure castor oil by repeated crystallisation (ten times) of the barium salt from alcohol, but the acid was still impure.

Substance.	Iodine value. Wijs. 2 hrs.	Bromine value. Solution. 2 hrs.	Iodine value. Calcd.	Br. value. Vapour. 5 mins.	Iodine value. Calcd.	Chlorine value. 5 mins.	Iodine value. Calcd.
Castor oil, A.	83.7	52.1	82.7	51.0 15 „ 56.2 30 „ 65.3 4 hrs. 68.8 maximum	81.0 89.2 103.6 109.2	24.3 25.0 31.3 37.1 7 hrs. 73.0 maximum	86.9 89.4 112.0 132.7 261.0
Castor oil, B.	84.8	50.1	79.6	48.8 15 „ 56.5 30 „ 58.2 4 hrs. 68.4	77.5 89.7 92.6 108.6	24.2 27.1 33.6 72.4 maximum	86.6 97.0 120.2 259.0
	(Theory 85.2) 2 hrs. 82.7 No increase for 18 hrs.	(Theory 53.7) 2 hrs. 51.9 No increase for 18 hrs.		5 mins. 56.8 15 „ 57.6 30 „ 61.6 maximum	90.0 91.4 97.8	(Theory 23.8) 5 mins. 20.1 15 „ 24.6 30 „ 28.0 7 hrs. 48.8 maximum	71.9 88.0 100.2 174.6
Ricinoleic acid			82.4				

The above results show that the halogen vapour absorptions are not comparable with the absorption obtained by Wijs method. The high results obtained are due, no doubt, to substitution which is probably accelerated by the presence of the hydroxyl grouping in the molecule.

RICINOLEIC ACID.—Two large films were brominated for 7 hours, and the resulting compound was dissolved in alcohol and reduced with dry hydrogen chloride gas and zinc dust for one hour. The mixture obtained was filtered and washed, and the hydrochloric acid and alcohol were evaporated. The resulting ester was hydrolysed with excess of potassium hydroxide in alcohol, and the fatty acid liberated in the usual manner. The final substance obtained had an iodine value (Wijs) of 80.0, and was probably the original ricinoleic acid used.

ARACHIS OILS.—It was found that the chlorine vapour method gave remarkably high results with arachis oil. The difference may prove to be of analytical value.

Arachis Oils and Fatty Acid.							
Substance.	Iodine value. Wijs. 2 hrs.	Br. value. Solution. 2 hrs.	Iodine value. Calcd.	Br. value. Vapour. 30 mins.	Iodine value. Calcd.	Chlorine value. 15 mins.	Iodine value. Calcd.
Arachis oil, A.	94.9	57.0	90.4	59.2	94.0	24.9 30 „ 29.1 40 „ 30.8 1 hr. 36.2 7 „ 48.1 maximum	89.1 104.0 110.2 129.5 172.0
Arachis oil, B.	86.2	51.7	82.0	54.3	86.2	28.2 30 „ 28.7 40 „ 30.7 1 hr. 34.9 7 hrs. 44.5 maximum	100.9 102.7 109.8 124.9 159.2
Fatty acid from B.	87.6	52.1	82.75	1 hr. 54.0	85.7	30 mins. 27.5 2 hrs. 29.3 7 „ 46.5 maximum All at 40° C.	98.4 104.9 166.3
Arachis oil, C. (extracted in the laboratory)	93.3	56.1	89.05	30 mins. 60.0	95.2	15 mins. 27.3 30 „ 28.3 40 „ 31.1 1 hr. 33.1 7 hrs. 49.0 maximum	98.0 101.2 111.3 118.2 175.3

It should be mentioned that, as the fatty acids were of a somewhat solid consistence, a higher temperature than usual was necessary for the vapour methods, to keep the film liquid and allow the absorption to take place.

EXPERIMENTS WITH DRY CHLORINE.—As there was a possibility that the high chlorine results obtained in the foregoing experiments might have been due to excessive substitution through the gas being wet (having been prepared from calcium hypochlorite, water and hydrochloric acid), the following three experiments were carried out, with the use of chlorine thoroughly dried through a large tower of freshly fused calcium chloride in small granules, sulphuric acid having been found unsatisfactory as a drying medium for such an active element.

		Chlorine value.	Iodine value.
Castor oil, A.	7 hrs. in dry chlorine,	72.5	= 259.4 (maximum).
Castor oil, B.	" " " " "	72.0	= 257.6 "
Arachis oil, A.	" " " " "	48.3	= 172.8 "

As can readily be seen, these results are almost identical with those previously obtained with "wet" chlorine, and the substitution is therefore due to the great chemical activity of the element, and not to the promoting action of moisture.

DIFFERENTIAL ABSORPTION AS A CRITERION OF CONSTITUTION.—Ponzio and Gastaldi (*Gazz. Chem. Ital.*, 1912, 42, 92; *ANALYST*, 1912, 37, 463) showed that when the double bond in an unsaturated fatty acid of the oleic series occurs next to the carboxyl group, absorption with Hübl, Wijs or Hanus solution is exceedingly slow, even taking two or three days. Experiments were therefore carried out with the following unsaturated acids of this and other groups:

Oleic acid (ordinary 9.10-oleic acid, B.D.H., redistilled), $\text{CH}_3(\text{CH}_2)_7\text{C}_{10}\text{H}=\text{C}_9\text{H}(\text{CH}_2)_7\text{COOH}$.

Parsley seed oil fatty acids free from essential oil, and unsaponifiable matter (mainly petroselinic acid, *viz.* isomeric 6.7-oleic acid) extracted from seeds in the laboratory.

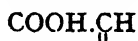
Petroselinic acid, $\text{CH}_3(\text{CH}_2)_{10}\text{C}_7\text{H}=\text{C}_6\text{H}(\text{CH}_2)_4\text{COOH}$.

Crotonic acid (B.D.H.), $\text{CH}_3\text{CH}=\text{CHCOOH}$, M.P. of sample 72° C.

Tiglic acid (B.D.H.), $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{COOH}$, M.P. of sample 65° C.



Maleic acid (B.D.H.) HC.COOH , M.P. of sample 140° C.



Fumaric acid (B.D.H.) H.C.COOH , sublimed at 200° C.

Cinnamic acid (synthetic), $\text{C}_6\text{H}_5\text{CH}=\text{CHCOOH}$, M.P. of sample 133° C.

Cinnamyl alcohol (B.D.H.) $\text{C}_6\text{H}_5\text{CH}=\text{CHCH}_2\text{OH}$, B.P. of sample 241° C.

Croton oil, A & B (A from B.D.H. with iodine value of 108.5).

Croton oil, B, fatty acids (*i.e.*, containing tiglic acid).

The pure organic acids were placed in small porcelain boats for the vapour absorptions.

Substance.	Iodine value. Wijs.	Bromine value. Solution.	Iodine value. Calcd.	Bromine value. Vapour.	Iodine value. Calcd.	Chlorine value.	Iodine value. Calcd.
Oleic acid	Theory 90.0 2 hrs. 85.1	Theory 56.7 2 hrs. 51.6	82.0	53.3	84.6	Theory 25.2 23.9	85.5
Parsley seed oil fatty acids	2 hrs. 102.3	2 hrs. 63.1	100.2	30 mins. 65.6	104.1	1 hr. 28.45	101.8
Crotonic acid†	Theory 295.4 18 hrs. 86.7 6 days 188.9 14 „ 190.3	Theory 186.0 18 hrs. 40.9	65.0	(M.P. 85° C.) 1 hr. 86.6*	296.2	Theory 82.6 2 hrs. 79.25† liquid	283.5
Tiglic acid	Theory 254 18 hrs. 47.0 3 days 96.6 No acid left for further expts.	Theory 160 18 hrs. 141.8	225.1	(M.P. 81.5° C.) 1 hr. 157.2*	249.7	Theory 71.0 2 hrs. 69.7† liquid	249.3
Maleic acid†	Theory 218.9 18 hrs. 2.2	Theory 137.9 18 hrs. 5.6	8.9	2 hrs. 9.0	14.3	Theory 61.2 6.5	24.4
Fumaric acid†	Theory 218.9 18 hrs. 15.6	Theory 137.9 18 hrs. 16.0	25.4	4 hrs. No absorption	—	4 hrs. No absorption	—
Cinnamic acid‡	Theory 171.6 18 hrs. 25.4 14 days 54.9 28 „ 65.5	Theory 108.1 18 hrs. 89.3 3 days 107.4	141.8 170.5	(M.P. 195° C.) 2 hrs. 107.2	170.2	Theory 48.0 2 hrs. 47.2 liquid	168.8
Cinnamyl alcohol	Theory 189.5 18 hrs. 135.6 No substance left.	Theory 119.4 18 hrs. 115.6	183.5	2 hrs. 107.2* liquid	170.2	Theory 52.9 2 hrs. 46.5† liquid	166.4
Croton oil, A.	2 hrs. 109.1 14 days 123.4 28 „ 123.7	2 hrs. 66.4	105.4	15 mins. 61.9 30 „ 71.2 1 hr. 73.8 7 „ 79.6 maximum	98.2 113.0 117.1 126.4	15 mins. 32.5 30 „ 38.0 1 hr. 41.0 7 „ 68.2 maximum	116.3 136.0 146.7 244.0
Croton oil, B.	2 hrs. 106.6 14 days 122.3 28 „ 122.8	2 hrs. 66.0	104.8	15 mins. 62.9 30 „ 70.5 1 hr. 70.8 7 „ 74.5 maximum	99.8 111.9 112.4 118.3	15 mins. 36.3 30 „ 36.5 1 hr. 37.8 7 „ 71.65 maximum	129.9 130.6 133.4 256.3
Croton oil, B.	2 hrs. 116.9 14 days 128.4	2 hrs. 69.6	110.5	30 mins. 73.5 1 hr. 74.1 7 „ 78.5 maximum	116.7 117.6 124.5	30 mins. 31.7 1 hr. 34.0 7 „ 70.5 maximum	113.4 121.6 251.9
Fatty acids	28 „ 128.9						

* These results were obtained by heating the bromine derivative at 60° C., to remove excess bromine, the compound being volatile at higher temperatures.

† These results were obtained by removing the excess chlorine in a vacuum desiccator. The crotonic and tiglic acid derivatives were volatile even under these conditions; hence the lower results.

‡ The iodine values (Wijs) obtained for these substances are similar to those obtained by Lewkowitsch (5th edition, Vol. I, 400), although the above figures are higher. It is worthy of note that the starch iodide end-points with this and the bromine solution method were very fugitive.

CROTON OIL.—The sample marked A was kindly supplied by British Drug Houses, who also gave its analysis as follows:—Sp. gr., at 15.5° C., 0.951; rotation, +10.6°; n_D^{40} , 1.4735; acid value, 22.4; saponification value, 209.4; and iodine value, 108.5.

The value obtained by me after 2 hours' absorption by the Wijs method was 109.1, and a similar result (106.6) was obtained with another sample.

It has been shown by Margosches (*Die Iodzahl-Schnellmethode und die Ueberiodzahl der Fette*, 1927, p. 12, 20) that by using a very large excess of halogen and continuing the absorption for a long period much higher iodine values are obtained with croton oil (e.g. 117.1 and 117.7). By continuing the absorption with the Wijs solution for 14 days and using 100 per cent. excess of the reagent, an iodine value of 123.4 was obtained with croton oil A, and a value of 122.3 with croton oil B. These results are thus in accordance with the theory of Ponzio and Gastaldi (*loc. cit.*), and may be explained by the presence of tiglic acid in the oil. On the other hand, the bromine vapour method gave results after 7 hours' absorption approximating those of Margosches.

As croton oil is an important drug in the British Pharmacopoeia, this anomaly in the iodine value is a point that should be recorded.

MALEIC AND FUMARIC ACIDS.—A 5 per cent. solution of each of these acids in pure glycerin was prepared, in an attempt to obtain higher bromine and chlorine vapour results, but the maleic acid solution gave the same result as the glycerin blank, and the fumaric solution precipitated on standing. No other suitable non-volatile solvent was found.

HYDROGENATED OILS AND THEIR FATTY ACIDS.—These are said to contain iso-oleic acids. According to Bauer (*Oil and Fat Ind.*, 1928, 5, 266) that of hydrogenated arachis oil is 12.13-oleic acid, $\text{CH}_3(\text{CH}_2)_4\text{CH}=\text{CH}(\text{CH}_2)_{10}\text{COOH}$. The following results were obtained with various hydrogenated oils and fatty acids:

Oil.	Iodine value. Wijs.	Br. value. Solution.	Iodine value. Calcd.	Br. value. Vapour.	Iodine value. Calcd.	Chlorine value.	Iodine value. Calcd.
Hydrogenated palm	2 hrs. 22.5	2 hrs. 13.85	22.0	30 mins. 15.3	24.3	30 mins. 7.9	28.3
Do. Fatty acids	2 hrs. 24.4	2 hrs. 18.1	28.7	30 mins. 16.8	26.6	15 mins. 8.0	28.7
Hydrogenated whale	2 hrs. 15.6	2 hrs. 9.8	15.6	30 mins. 8.75	13.9	30 mins. 4.0	14.3
Do. Fatty acids	2 hrs. 15.9	2 hrs. 10.1	16.0	30 mins. 11.0	17.5	30 mins. 4.6	16.4
Hydrogenated maize	2 hrs. 38.5	2 hrs. 24.2	38.4	30 mins. 23.8	37.8	45 mins. 11.5	41.1
Do. Fatty acids	2 hrs. 39.5	2 hrs. 24.25	38.7	1 hr. 23.7	37.6	45 mins. 11.4	40.8

For the bromine vapour and chlorine absorptions in the above series, the substances were used in a finely divided solid condition in small porcelain boats,

the melting points being high compared with previous oils and fats used. In these absorptions also, slightly variable results were obtained, due to substitution, which appears to occur somewhat readily with hydrogenated oils.

The fairly close agreement between the Wijs results and the bromine vapour results suggest that the iso-oleic acids present in these hydrogenated oils are not 2-3 oleic acids.

SUMMARY AND CONCLUSIONS.—From the foregoing experiments it can be claimed that the bromine vapour method for determining the degree of unsaturation of an oil or fat compares very favourably with the method of Wijs, usually being much more rapid (particularly with croton oil), and in many cases more nearly complete. The exceptions are castor oil and its predominant acid (ricinoleic acid), which readily undergo substitution with bromine vapour, such substitution presumably being caused by the presence of a hydroxy grouping in the molecule. The differences obtained for one hour's absorption with the two reagents (Wijs and bromine vapour) probably enable a judgment to be formed as to the position of the unsaturated bond in the fatty acids of the oleic series. The bromine vapour method also has a great advantage over others used, as it can be successfully employed when only small quantities of material are available. (Not more than 0.025 grm. of substance was used in any of the above gravimetric experiments.)

The chlorine vapour method, when applied to oils and fats, in most cases gives results which are too high, owing to the substitution caused by the greater chemical activity of this element, as previously stated. Such substitution, however, appears to reach a limit.

Although primarily concerned with oils and fats, this work was extended to other unsaturated organic substances, and the experiments made, both with bromine and chlorine vapours, show that results agreeing closely with theory can be obtained, except with maleic and fumaric acids, which are evidently very inert under this treatment. This method could, therefore, be successfully used to determine the amount of unsaturated compounds present in admixture with saturated substances.

The results obtained for oils and fats with bromine in acetic acid solution are not satisfactory, the figures usually being lower than those obtained with Wijs solution, probably owing to the formation of bromhydrins during the absorption. This method, however, shows promise with the other organic substances used, but is not to be compared with the vapour absorption results obtained.

In conclusion, I should like to thank Dr. Toms for his help and interest in these experiments, Dr. Mitchell for his helpful suggestions throughout the experimental period, and the Directors of Messrs. Loders and Nucoline, Ltd., for the use of their laboratory for practically the whole of the work.

DISCUSSION.

Mr. E. R. BOLTON referred to the many methods which had been used or proposed in past years to determine the iodine value. He expressed the opinion that the Wijs method had been clearly established as giving a definite measure of

the unsaturated oils of a simple type, but no method was absolutely satisfactory in the case of highly unsaturated or complex bodies. It now seemed that the application of the bromine method was likely to supply a better differentiation than had been possible hitherto. If the figures given in the paper were plotted out and carefully studied, they might lead to a new way of arriving at the nature of the unsaturated acids present. It was impossible to criticise or discuss the wonderful mass of figures put before the Society, but he was very much impressed with the way they had fitted into theory.

Mr. C. A. MITCHELL thought that the paper was very valuable from the point of view of developing a new aspect of halogen absorption. Many years ago Lewkowitsch had said that he was thankful he had not added another method to the methods of iodine absorption—he rather implied that the Wijs method was the last word in iodine absorption, and that nothing further could be done. However, even Wijs himself had recently admitted that his method did not hold good for such acids as mentioned in this paper, although if continued long enough it would be possible to get better results; but even then there was a risk of decomposition of the reagent. He was not sure whether Mr. Croxford had taken precautions to eliminate moisture from the chlorine.

Mr. E. J. LUSH remarked that in all these halogen absorptions there was a certain risk of substitution. One element which had not been mentioned was hydrogen, and the determination of the hydrogen number might add a confirmatory method free from the danger of substitution.

Mr. K. A. WILLIAMS demonstrated by means of curves the progress of the iodine absorption with reference to time, and showed it to occur in two stages, the first being rapid and the second very slow. For most oils the beginning of the second stage was well defined and corresponded to the Wijs iodine value of the oil. In the case of tung oil, however, the change from the first to the second stage was gradual, and the apparent iodine value was consequently somewhat indefinite. He suggested that the real iodine value would be given by the point of intersection of the lines representing the two stages of absorption.

Dr. H. TOMS, replying on behalf of the author, referred to the question of bromhydrin formation during the determination of unsaturation by means of bromine solution, and said that this was very unlikely to occur, since water (as a solvent for potassium iodide) was added only at the end of the absorption period in order to titrate the excess of bromine. Of course, when bromine vapour was used the possibility of bromhydrin formation did not occur, since water was not present.

In the case of chlorine the corresponding possibility had occurred to Mr. Croxford in the later stages of the work, for the chlorine used was obtained from bleaching powder and was necessarily damp. This might account for the fact that some of the values obtained by chlorine absorption were not so satisfactory as those obtained by the use of dry bromine vapour. Throughout the whole of the work Mr. Croxford and he had had in mind the possibility of substitution occurring simultaneously with the direct addition, but unfortunately no satisfactory means of settling this point had, as yet, suggested itself. In most cases it appeared that bromine vapour gave complete saturation in a few minutes.

In reply to Mr. Williams, Dr. Toms assumed that the phrase "true iodine value" meant the maximum theoretical absorption obtainable for the complete saturation of the double bonds and not the maximum value obtainable under the specified conditions of some standard method, such as that of Wijs or Hübl, which, as was now known, did not necessarily give figures representing complete saturation.

One important point had emerged from Mr. Croxford's work, namely, that the position of the double bond in the fatty acid molecule exerted a pronounced influence on the absorption of iodine as determined by the Wijs method. Thus one could not say when a Wijs test was finished, *i.e.* when the oil was completely saturated with iodine chloride. He (Dr. Toms) had entirely overlooked this position effect, although he had shown that the combination of double bonds present in a molecule exerted a profound influence on halogen absorption. This was pre-eminently so in the case of tung oils, for which, for many years, figures representing only about two-thirds of the real unsaturation value of these oils had been accepted as correct, although it had now been proved that the older values did not represent complete absorption:

Investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates.

XV. A New Method for the Separation of Tantalum and Niobium from Titanium and Zirconium (1 : Qualitative).

By W. R. SCHOELLER, Ph.D.

THE separation of tantalum, niobium, titanium, and zirconium (with hafnium) is, no doubt, the central and most difficult problem of earth-acid analysis. Its solution is of practical importance to the mineralogist, as a number of rarer earth-acid minerals contain titania and zirconia in substantial proportions; many of the published analyses of such minerals can only be regarded as rough approximations. Other tantaloniobate minerals contain small to minute amounts of the dioxides.

The complexity of the problem will be better understood when it is borne in mind that the quantitative separation of the three binary mixtures, ($Ta_2O_5:Nb_2O_5$), ($M_2O_5:ZrO_2$), and ($M_2O_5:TiO_2$), in any proportions, has only recently been made reasonably accurate (Sections IV, V, ANALYST, 1925, 50, 485, 494; IX, *id.*, 1927, 52, 633; XIII, *id.*, 1928, 53, 515; and XIV, *id.*, 1929, 320). The resolution of the ternary mixture ($M_2O_5:TiO_2:ZrO_2$) into its constituents is accounted difficult enough even as a proposition of qualitative analysis. It involves a preliminary splitting up into simpler groups, such as (a) ($M_2O_5+TiO_2$): ZrO_2 ; (b) ($M_2O_5+ZrO_2$): TiO_2 ; or (c) $M_2O_5:(TiO_2+ZrO_2)$. *Grouping* (a) was wrongly held to be the result of bisulphate fusion followed by boiling of the solution of the melt (XII, ANALYST, 1928, 53, 472). *Grouping* (b) is what Noyes and Bray (*A System of Qualitative Analysis for the Rare Elements*; New York, 1927; Procedure 41, p. 98) claim to be able to accomplish by extraction of the precipitated hydroxides with sodium salicylate and salicylic acid. This method, which I have come to regard as ineffective, will be criticised at greater length in the concluding paragraph of this paper. *Grouping* (c) was believed by the earlier mineralogists to take place when

the bisulphate melt of the oxides is extracted with cold water or dilute acid. The procedure is now known to be utterly unreliable (*cf.* Sect. XII, *loc. cit.*).

AUTHOR'S INVESTIGATION.—The object of the present investigation was to work out a reliable qualitative method before attempting the quantitative separation under discussion. After experimenting with several schemes I had the good fortune to discover a method which not only makes the identification of the elements in question a surprisingly simple operation, but is also expected to provide the basis for their quantitative separation. This Section contains the directions for the qualitative separation method and a preliminary notice of its application for quantitative purposes.

CHEMISTRY OF THE PROCESS.—The new process is an application of certain principles of colloid chemistry. The dioxides TiO_2 and ZrO_2 are capable of forming definite sulphates relatively stable in aqueous solution, whilst the pentoxides Ta_2O_5 and Nb_2O_5 do not form salts. As mentioned above under *Grouping (c)*, the earliest attempts at a separation, *i.e.* extraction of the bisulphate melt with cold water, were based on this fundamental difference in chemical deportment. What makes the separation ineffective is the pronounced tendency of the reacting elements to form complexes with each other, the result of association being a profound alteration of the specific properties of the pure compounds. This constitutes "loss of individuality" (Crookes). Hence, when the bisulphate melt is extracted with cold water or dilute acid no separation takes place, the titania and earth acids distributing themselves more or less evenly over the solution and the residue; zirconia accentuates the solvent effect of titania upon the earth acids.

Now it occurred to me to attempt to treat the bisulphate melt with a reagent that would prevent complex-formation. Tannin having been used in the course of these investigations as an effective precipitant of the earth acids, it was surmised that they would remain insoluble upon treatment of the melt with a tannin solution containing sufficient sulphuric acid to act as a solvent for the sulphates of titanium and zirconium. In the light of colloid theory, when the bisulphate melt is in contact with a tannin dispersion, the small particles of the molecularly-dispersed sulphates of potassium, titanium, and zirconium would be able to diffuse through the mesh-like structure of the liquid phase, whereas the larger aggregates of tantalic and niobic acid would be entangled and coagulated by the tannin sol as soon as they were formed during the disintegration of the melt.

These deductions were verified experimentally and fully confirmed. Extraction of the bisulphate melt with 5 per cent. sulphuric acid containing 1 per cent. of tannin yields a solution of titanium and zirconium sulphates and a residue consisting of the brightly-coloured tannin adsorption-complexes of the earth acids. To use Crookes's terminology, the addition of tannin restores the individuality of the elements.

The new method will hereafter be termed the "pyrosulphate and tannin method."

THE SEPARATION.—The mixed oxides (0.1 to 0.2 grm.) are fused with 2 to 3 grms. of bisulphate in a silica crucible. The melt is made to solidify in a thin layer around the sides of the crucible. The hot reagent (1 grm. tannin dissolved in 90 c.c. of water and 10 of 1:1 sulphuric acid) is poured into the crucible, which is gently heated with a moving bare flame, the melt disintegrating into small detached fragments. The contents of the crucible are transferred to a 400 c.c. beaker, and the crucible rinsed with the rest of the reagent. The liquid is heated to boiling, and then left on a hot plate or water-bath until it is clear and the precipitate has coagulated (roughly, 15 minutes). The precipitate, *TP*, is filtered off, and the filtrate collected in a conical flask.

Identification of Titanium and Zirconium.—The filtrate is boiled down rapidly with 5 c.c. of strong sulphuric acid until it darkens and foams. It is then treated with small portions of strong nitric acid till it becomes clear and colourless. The tannin is very readily oxidised, the operation taking only a few minutes. The liquid is then heated over a bare flame until copious white fumes are given off, another drop or two of nitric acid being added, if necessary, to bring about complete decolorisation. After cooling, 50 c.c. of cold water are added, and the titanium and zirconium identified by known methods: the solution is treated with an excess of hydrogen peroxide, the familiar yellow to orange colour proving the presence of titania. Zirconia is next detected by addition of a large excess of ammonium phosphate, which precipitates flocculent colourless zirconium phosphate.

Identification of Tantalum and Niobium.—The precipitate *TP* has a buff to bright scarlet colour, according to the composition of the oxide mixture. Its formation proves the presence of the earth acids; the subsequent procedure here given serves for their separate identification. It may be added that *TP* is quite different from the flocculent, extremely voluminous tannin complexes obtained by precipitation: it is remarkably compact, and in part retains the shape of the fragments of the melt if the mixed oxides contain much earth acid.

Even if the joint detection of the earth acids is sufficient for the purpose of the qualitative analysis, I would advise operators not too familiar with the subject to proceed with the next stage, as it provides an unmistakable confirmatory test.

The precipitate *TP* is well washed with 2 per cent. sulphuric acid containing a little tannin, ignited, fused with bisulphate, and the melt dissolved in a hot, strong solution of tartaric acid. The liquid is suitably diluted (20 c.c. for 0.01 grm. of pentoxides), and treated while boiling with one-fifth of its bulk of strong nitric acid; a white, flocculent precipitate *HP*, forming either at once or after short boiling, is a certain proof of the identity of the earth acids. This procedure is the tartaric hydrolysis method fully described in Section XIV (ANALYST, 1929, 321).

For the separate identification of tantalum and niobium, the precipitate *HP* is collected, ignited, fused with bisulphate, the product dissolved in ammonium oxalate solution, and the latter submitted to Powell and Schoeller's tannin method described in Section V (ANALYST, 1925, 50, 495).

If the titania content of the oxide mixture is found to be low, the procedure for identifying tantalum and niobium may be shortened: the tannin precipitate *TP* is ignited and treated by Powell and Schoeller's process without having to pass through the *HP* stage. If, on the other hand, the mixed oxides are rich in titania, the tartaric hydrolysis is advisable, as it frees *TP* from a slight contamination with titania, which might otherwise discolour the yellow tantalum precipitate (Section XI, ANALYST, 1928, 53, 265).

RESULTS OF TEST SEPARATIONS.—In order to demonstrate the efficacy of the method, I analysed 13 oxide mixtures, the composition of which was not disclosed to me till after the conclusion of the work. The composition of the mixtures was varied in such a manner as to present the greatest diversity, from the total absence of each constituent to its forming the bulk of the mixture. Let *M* and *m* represent large and small amounts of M_2O_5 , respectively; *T* and *t*, large and small amounts of TiO_2 ; *Z* and *z*, large and small amounts of ZrO_2 . These values were permuted in the following manner:

Binary mixtures: *mT*; *Tz*; *mZ*; *tZ*; *Mt*; *Mz*.

Ternary mixtures: *mTz*; *mtZ*; *Mtz*.

mTZ; *MTz*; *MtZ*. *MTZ*.

The cases *MT*; *MZ*; and *TZ* were disregarded as superfluous. The mixtures were not analysed in the order given, but chosen at random (*vide infra*, Quantitative Separation). In all cases the composition was ascertained correctly without any difficulty within two hours. The time taken does not include the separate identification of tantalum and niobium; this part of the process having been exhaustively treated in Section V (*loc. cit.*), I felt justified in saving myself the time and labour it would have entailed.

TARTARIC HYDROLYSIS AS AN IMPORTANT EARTH-ACID TEST.—While the detection of the earth acids is under consideration, I must call attention to the great practical value of tartaric hydrolysis as a distinctive reaction of tantalum and niobium. It need hardly be pointed out that precipitation of a hydrated oxide by a mineral acid from a tartrate solution is a novel and peculiar reaction. On theoretical grounds we may say that it cannot take place with metals that form soluble nitrates or chlorides; it must be confined to those more electro-negative elements the hydroxides of which are insoluble in the mineral acid used: the reaction might possibly be given also by antimony, tin, germanium, and tungsten. This deduction was verified by experiment, with the following results:

	Nitric acid.	Hydrochloric acid.
Antimony (1).	No ppt.	No ppt.
Tin (2).	White flocculent ppt.	No ppt.
Germanium (3).	No ppt.	No ppt.
Tungsten (4).	Yellow ppt.	Yellow ppt. (5).

(1) $NaSbO_3$ (1 grm.) dissolved in tartaric and a little sulphuric acid; boiled with 30 c.c. mineral acid in 200 c.c. bulk. (2) Na_2SnO_3 , as (1). (3) GeO_2 (0.03 grm.) dissolved in $NaOH$; a few drops H_2SO_4 ; 0.25 grm. $C_4H_6O_6$; boiled with 5 c.c. mineral acid. (4) WO_3 fused with $KHSO_4$; dissolved melt in $C_4H_6O_6$. (5) No ppt. in dilute solution.

Specificity.—It appears, then, that stannic acid is the only other substance giving the same reaction as the earth acids when nitric acid is used; hydrochloric acid gives no precipitate, stannic chloride being soluble. Now, as stannic oxide is hardly soluble in bisulphate, and the dissolved part removable from the tartrate solution by hydrogen sulphide (Sect. I, ANALYST, 1922, 47, 93), we may conclude that the formation of a white precipitate under the above conditions is a specific reaction of tantalum and niobium.

Sensitiveness.—Quantitative tests demonstrating the sensitiveness of the reaction and the recovery of small amounts of earth acid, both in presence and absence of titania, are given on p. 321 of Section XIV (ANALYST, 1929). A conservative estimate, based on those tests, gives a sensitiveness of the order of 0.03 mgrm. M_2O_5 per c.c., the test being unaffected by five times that amount of titania; zirconia, if present in such proportions, should be previously removed by the pyrosulphate and tannin method (this Section).

Mineralogical Application.—The test should prove a valuable adjunct in determinative mineralogy. The powder is fused with bisulphate, and the product dissolved by boiling with strong tartaric acid solution. The (filtered) liquid, boiled with one-fifth its bulk of strong hydrochloric acid, furnishes a white flocculent precipitate of tantalalic and niobic acids. Betafite, euxenite, and stibiotantalite (0.02 grm. each), tested in this manner, readily gave a positive reaction.

IMPORTANT EARTH-ACID TESTS.—It is concluded that tartaric hydrolysis is a specific, as well as a sensitive and convenient, test for the joint detection of tantalum and niobium, applicable in presence of the more electropositive, or salt-forming, elements. It will be useful here to append a list of the most important reliable earth-acid reactions, as this subject continues to receive but scant attention in analytical text-books.

(a) *Reactions for their Joint Detection.*—(1) Tartaric hydrolysis (this Section); (2) precipitation of the crystalline sodium salts (VI, ANALYST, 1926, 51, 615); and (3) precipitation of the earth acids from solutions of 4:3 potassium tantalate and niobate by acetic or mineral acids.

(b) *Reactions for their Separate Identification.*—

	Tantalum.	Niobium.
(4) Tannin in oxalate solution.	Sulphur-yellow ppt.	Red ppt.
(5) Zinc dust in phosphoric acid solution.	No coloration.	Dark to black coloration.
(6) KF in fluoride solution.	Crystalline ppt.	No ppt.
(4) Section V, <i>loc. cit.</i>	(5) Giles, <i>Chem. News</i> , 1907, 95, 1.	(6) Marignac's method.

Finally, it may be pointed out that Rose (*Traité Complet*, 1859) correctly describes the tantalum-tannin precipitate as being light yellow (*jaune clair*); whereas most modern text-books give yellow-brown or light brown. Such a precipitate, however, indicates that the tantalalic acid contains titania (XI, *loc. cit.*).

QUANTITATIVE SEPARATION OF THE EARTH ACIDS FROM TITANIA AND ZIRCONIA (PRELIMINARY NOTICE).—The quantitative possibilities of the pyro sulphate and tannin method were investigated, simultaneously with its qualitative application, by means of the 13 test separations described above.

All the pentoxide precipitates *TP* were washed, ignited, and weighed. Titania and zirconia, if subordinate, were actually determined, the former colorimetrically, the latter gravimetrically as pyrophosphate (Lundell and Knowles, *ANALYST*, 1920, 45, 28); if present in large amount, they were taken by difference, the total weight of mixed oxides taken, and that only, being known to me: quantities computed by difference are shown in *italics*. The numbering of the experiments indicates the order in which the "unknown" mixtures were received. The pentoxide preparation used contained 61.4 per cent. Ta_2O_5 and 38.6 per cent. Nb_2O_5 :

Type.	Exp.	M_2O_3		TiO_2		ZrO_2	
		Taken. Grm.	Found. Grm.	Taken. Grm.	Found. Grm.	Taken. Grm.	Found. Grm.
<i>mT</i>	7	0.0058	0.0077	0.0922	<i>0.0903</i>	nil	nil
<i>Tz</i>	4	nil	nil	0.0946	<i>0.0937</i>	0.0058	0.0067
<i>mZ</i>	12	0.0072	0.0070	nil	nil	0.1054	<i>0.1056</i>
<i>tZ</i>	11	nil	nil	0.0052	0.0056	0.0965	<i>0.0961</i>
<i>Mt</i>	8	0.0900	0.0900	0.0033	0.0055	nil	nil
<i>Mz</i>	9	0.0925	0.0894	nil	nil	0.0050	0.0060
<i>mTz</i>	10	0.0050	0.0046	0.0950	<i>0.0946</i>	0.0092	0.0100
<i>mtZ</i>	2	0.0054	0.0042	0.0056	0.0055	0.0936	<i>0.0949</i>
<i>Mtz</i>	13	0.0908	0.0900	0.0030	0.0020	0.0044	0.0043
<i>mTZ</i>	1	0.0054	0.0046	0.0709	<i>0.0686</i>	0.0708	0.0739
<i>MTz</i>	3	0.0723	0.0757	0.0716	<i>0.0673</i>	0.0050	0.0059
<i>MtZ</i>	6	0.0704	0.0720	0.0054	0.0044	0.0736	<i>0.0730</i>
<i>MTZ</i>	5	0.0620	0.0625	0.0643	<i>0.0603</i>	0.0628	0.0663

It must be understood that no attempt has been made at introducing any analytical refinements, the idea being merely to ascertain the qualitative composition of the oxide mixture, supplemented by a rapid exploratory quantitative analysis for purposes of orientation. Under these circumstances it will, I think, be conceded that the results are, on the whole, very gratifying, and justify my confidence in the ultimate success of the method as a strictly quantitative process.

A few supplementary remarks may here be added. The zirconium phosphate precipitate was mixed with a large proportion of filter pulp, so as to expedite filtration and washing with dilute ammonium nitrate solution; except in two cases, the ignited zirconium pyrophosphate was dark grey to black, and the error positive: "black residues of excessive weight," to quote Lundell and Knowles (*loc. cit.*). The approximate factor 0.46 was used for the conversion $ZrP_2O_7:ZrO_2$ (Lundell and Knowles' factor is 0.4632). As the constant association of zirconium and hafnium has now been proved, the mixed oxides $(Zr,Hf)O_2$ should be determined as such. For this, if for no other reason, I intend confining the use of the phosphate method to the qualitative and preliminary quantitative analyses as outlined in this Section.

A THIRD METHOD FOR THE SEPARATION OF TITANIA FROM THE EARTH ACIDS.—

The particulars here given make it fairly clear that the utility of the pyrosulphate and tannin method is not necessarily confined to the separation to which it was first applied. In particular, the procedure may yet prove a valuable adjunct for the separation of titania from the earth acids, along with the tartaric hydrolysis and oxalate salicylate methods (IX and XIV, *loc. cit.*). The question will be investigated at an early date.

OBSERVATIONS ON THE SALICYLATE PROCESS.—Noyes and Bray (*op. cit.*, pp. 76–81, 98–99) separate titanium from tantalum, niobium and zirconium by boiling the mixed hydroxides with 5 grms. of sodium carbonate and 15 grms. of salicylic acid in a total bulk of 400 c.c. for two hours, replacing the water lost by evaporation. They express themselves as follows (p. 77): “We have found that, by applying this process to the precipitated hydroxides . . ., all the titanium passes into solution, and that all the tantalum, columbium, and zirconium remain undissolved, whether the elements are present in large or small quantity, and whether they are alone or mixed.” The salicylate process would thus afford a means not only for the qualitative, but even for the quantitative separation of titania from the other oxides in one operation. My own experience being quite at variance with that of Noyes and Bray, it is necessary here to record my observations.

(1) Prior to the publication of Noyes and Bray’s work, Schoeller and Deering (IX, Table III, p. 630, *loc. cit.*) had conducted a series of experiments with an almost identical process in an endeavour to separate titania from the earth acids. They were unable to extract more than 80 per cent. of the titania in one operation; “even a third treatment failed to effect its complete removal. Moreover, niobic acid did not remain altogether insoluble.” With low $\text{TiO}_2:\text{M}_2\text{O}_5$ ratios, the titanium extraction was poorer still (about 50 per cent.).

(2) During the initial stages of the present investigation, the appearance of Noyes and Bray’s book caused me to re-investigate the subject of salicylate extraction. This time I experimented with mixtures of titania and zirconia. Nine tests were carried out:

Exp.	TiO_2 taken. Grm.	ZrO_2 added. Grm.	TiO_2 in		Remarks: See below.
			1st extract. Grm.	2nd extract. Grm.	
1	0.1020	0.1018	0.0390	—	} (a)
2	0.1035	0.1048	0.0376	—	
3	0.1130	0.1450	a few mgrms.	—	} (b)
4	0.1364	0.1037	do.	—	
5	0.1560	0.1348	0.0280	0.0235	} (c)
6	0.1252	0.1585	0.0197	0.0183	
7	0.1027	0.1026	0.0288	—	} (d)
8	0.1068	0.1040	0.0319	—	
9	0.1000	0.1203	0.0385	—	(e)

The mixed oxides were fused with bisulphate, the acid solution of the melt precipitated with ammonia, the precipitate collected and washed with dilute ammonium nitrate solution. Various modifications of the procedure were then tried: (a) The precipitate was treated in strict accordance with Noyes and Bray's above directions. (b) The precipitate was dissolved in 2 c.c. of strong nitric acid, and the solution slowly poured into a boiling solution of 5 grms. of sodium salicylate in 500 c.c. of water. (c) The ignited residue from the extraction of the precipitate with sodium salicylate (5 grms.) and salicylic acid (2 grms.) was re-treated. (d) Sodium salicylate was used in Exps. 7, the ammonium salt in 8: 5 grms. of salicylate, 2 of salicylic acid, bulk 400 c.c.; boiled one hour. (e) The solution of the bisulphate melt was neutralised with sodium bicarbonate and slowly poured into a boiling solution of 5 grms. of sodium salicylate in 40 c.c. water; final bulk, 200 c.c.

These brief notes suffice to show, not only that Noyes and Bray's results could not be reproduced, but also that the extraction was almost uniformly poor and much lower still than in Schoeller and Deering's experiments with titania and the earth acids. I have become convinced that a molecularly-admixed constituent of a complex precipitate cannot be extracted quantitatively by a process of selective solution: the history of analytical chemistry, particularly that of the earth acids and the platinum metals, teems with instances of faulty methods based on that principle.

SUMMARY.—A new process (the "pyrosulphate and tannin method") is described for the qualitative separation of tantalum and niobium from titanium and zirconium. It consists in fusing the mixed oxides with bisulphate and extracting the fusion product with 5 per cent. sulphuric acid containing one per cent. of tannin. The earth acids remain insoluble as coloured tannin adsorption complexes, whilst the sulphates of titanium and zirconium dissolve. The addition of the tannin prevents the formation of complexes, which render the separation ineffective when the bisulphate melt is leached with cold water or dilute acid.

The most reliable tests for tantalum and niobium are discussed: it is shown that the precipitation of the earth acids from boiling tartrate solutions by excess of mineral acid is a specific, sensitive, and convenient earth-acid reaction applicable in presence of other metals. A preliminary notice is given of the quantitative application of the pyrosulphate and tannin method. The salicylate process for the separation of titanium from tantalum, niobium, and zirconium is adversely criticised.

I have much pleasure in acknowledging my indebtedness to Dr. Ludwig Moser, Professor of Analytical Chemistry in the Polytechnic University of Vienna, for courteously placing at my disposal the preparation of pure germanium dioxide used in this investigation.

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Experiments on Quantitative Oxidation with Ceric Sulphate.

By A. J. BERRY, M.A.

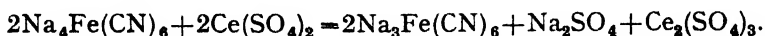
ALTHOUGH the powerful oxidising properties of ceric sulphate have long been known, little use appears to have been made of them for analytical work until quite recently. Benrath and Ruland (*Z. anorg. Chem.*, 1920, 114, 267) have described some experiments on the oxidation of various compounds by ceric sulphate, and detailed investigations on the use of this oxidising agent in potentiometric titration analysis have been published by Furman (*J. Amer. Chem. Soc.*, 1928, 50, 755, 1675, and 51, 1128, by Willard and Young (*ibid.*, 1928, 50, 1322, 1334, 1368, 1372, 1379, and 1929, 51, 139), and by Atanasiu and Stefanescu (*Ber.*, 1928, 61, 1343). Very few experiments have been described with ceric sulphate as a volumetric oxidising agent, apart from potentiometric methods for determining the end-point, but mention should be made of the titration of ferrous salts in conjunction with diphenylamine as an internal indicator (Willard and Young). The observations of previous investigators as regards the stability and highly oxidising properties of solutions of ceric sulphate have been verified by the experiments of the writer, so far as the work has overlapped; in particular, reference may be made to the quantitative oxidation of vanadyl salts, nitrites and ferrocyanides.

PREPARATION AND STANDARDISATION OF SOLUTIONS OF CERIC SULPHATE.—Meyer and Aufrecht (*Ber.*, 1904, 37, 140) have shown that ceric oxide, when treated with concentrated sulphuric acid, is converted quantitatively into ceric sulphate without passing into solution. The product is, however, readily soluble in water, the liquid having a deep orange colour. In my experiments the solutions were prepared from ceric nitrate, the salt being heated with excess of concentrated sulphuric acid in an evaporating dish, with frequent stirring, until qualitative tests showed the complete elimination of nitric acid. The resulting product, containing free sulphuric acid, was then diluted with water, and, after attaining a steady temperature, standardised with reference to its available oxygen. It was found that solutions of ceric sulphate of the order of $N/10$ concentration could be readily prepared by treating 25 grms. of ceric nitrate with concentrated sulphuric acid in this way, and diluting the resulting aqueous solution to 500 c.c.

The available oxygen in such a solution may be standardised by reaction with various suitable reducing agents, such as ferrous ammonium sulphate. If this salt is used, the end-point of the reaction can be determined in the usual way with potassium ferricyanide as an external indicator, or, more conveniently, with a few drops of a 1 per cent. solution of diphenylamine in concentrated sulphuric acid as an internal indicator. In any case, as in all volumetric work,

it is very desirable to standardise the reagent under conditions as similar as possible to those in which it is to be employed.

OXIDATION OF FERROCYANIDES.—This reaction takes place readily at the ordinary temperature, the end-point of the reaction being determined accurately by means of diphenylamine sulphate:



The following results may be quoted by way of illustration.

The concentration of a solution of sodium ferrocyanide was determined in the first instance by a standard solution of potassium permanganate containing 0.769 grm. of available oxygen per litre.

Fifty c.c. of the ferrocyanide solution required 33.75 c.c. of the potassium permanganate solution, and hence contained 19.6 grms. of sodium ferrocyanide (calculated as anhydrous salt) per litre.

Fifty c.c. of the ferrocyanide solution, diluted to about 300 c.c. and containing a few drops of a 1 per cent. solution of diphenylamine in concentrated sulphuric acid, required 28.55 c.c. of a solution of ceric sulphate. Thus the ceric sulphate solution contained 0.909 grm. of available oxygen per litre, and the sodium ferrocyanide solution contained 19.7 grms. of the salt (anhydrous) per litre.

In another experiment, in which a solution of ceric sulphate containing 0.844 grm. of available oxygen per litre was used, 50 c.c. of the sodium ferrocyanide solution required 30.75 c.c. of ceric sulphate. The calculated value of the concentration was identical with that of the previous experiment, *viz.* 19.7 grms. of sodium ferrocyanide per litre.

OXIDATION OF TARTRATES.—Benrath and Ruland (*loc. cit.*) studied the oxidation of tartaric acid by ceric sulphate in hot aqueous solution, and concluded that the reaction, which proceeds somewhat slowly, takes place as follows:—



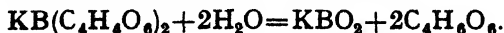
One molecule of tartaric acid requires, therefore, four atoms of available oxygen for conversion into carbon dioxide and formic acid, the latter resisting further oxidation. In my experiments the reaction was found to proceed somewhat differently, two molecules of tartaric acid requiring seven atoms of available oxygen, thus:



A solution of tartaric acid, containing 2.31 grms. of the acid per litre, as determined by titration with standard sodium hydroxide (phenolphthalein as indicator), was titrated with a solution of ceric sulphate containing 0.956 grm. of available oxygen per litre, 25 c.c. of the tartaric acid solution reacting with 22.6 c.c. of the ceric sulphate solution. From these numbers it follows that one molecular proportion of tartaric acid requires 3.51 atomic proportions of available oxygen.

This reaction was applied to determine the reacting weight of a potassium borotartrate, $\text{KB}(\text{C}_4\text{H}_4\text{O}_6)_2$, recently prepared by Professor Lowry (unpublished

observation). The calculated molecular weight of the compound is 346, and the aqueous solution is acid in consequence of hydrolysis:



When titrated with *N*/10 sodium hydroxide solution, with phenolphthalein as indicator in presence of mannitol, an equivalent weight of 88.4 was found. With methyl red as indicator without mannitol, a value of 122 was determined for the equivalent weight.

A solution containing 8.842 grms. of the salt per litre was titrated with a solution of ceric sulphate corresponding to 0.956 gm. of available oxygen per litre. Twenty c.c. of the potassium borotartrate solution reacted with 62.5 c.c. of ceric sulphate. Assuming that one molecular proportion of the salt requires seven atomic proportions of available oxygen for oxidation by ceric sulphate, the value found for the molecular weight was 332.

ANALYSIS OF THALLOUS SALTS.—Under ordinary conditions ceric sulphate is without action upon dilute aqueous solutions of thallous salts. In the presence of a very high concentration of hydrochloric acid, however, the ceric salt acts like potassium iodate (Berry, *ANALYST*, 1926, **51**, 137), and quantitative oxidation to the thallic condition can be realised.

In order to apply this reaction to the determination of thallous salts, a solution of iodine in chloroform is converted quantitatively into iodine monochloride to furnish a means for determining the end-point. A few c.c. of a dilute solution of iodine in chloroform are placed in a stoppered bottle, about 50 c.c. of concentrated hydrochloric acid (free from traces of chlorine) are added, and the solution of ceric sulphate delivered cautiously from a burette, with frequent shaking, until the violet colour of the chloroform just vanishes. A measured volume of the solution of the thallous salt is then added to the liquid, and the standard solution of ceric sulphate run in, again with frequent shaking, until the chloroform is once more rendered colourless.

A solution of ceric sulphate for determining thallous salts must be standardised in the way in which it is to be used, and not as, for example, in the titration of ferrocyanides with diphenylamine as indicator, as otherwise errors of the order of two or three per cent. may be involved. Standardisation can, however, be readily effected by oxidising a solution of potassium iodide of known concentration to iodine monochloride, thus:



Twenty c.c. of a solution of potassium iodide, containing 7.042 grms. of the salt per litre, required 18.7 c.c. of a solution of ceric sulphate. The concentration of the solution of ceric sulphate, in terms of available oxygen, was 0.819 gm. of available oxygen per litre.

A solution of thallous sulphate containing 30 grms. of the salt per litre, as determined by direct titration with potassium iodate, was titrated with ceric sulphate in the manner described, 10 c.c. of the thallous sulphate solution requiring

23.3 c.c. of ceric sulphate for complete oxidation. From this experiment it follows that the concentration of the solution was 30.05 grms. of thallous sulphate per litre.

THALLIUM TRI-IODIDE (compare Berry and Lowry, *J. Chem. Soc.*, 1928, p. 1748.)—When 0.342 gm. of the compound was titrated with ceric sulphate, as described above, the calculated weight was 0.349 gm. With the use of potassium iodate, 0.261 gm. of the compound gave a titration value of 0.264 gm.

CHEMICAL LABORATORY
(GOLDSMITHS' METALLURGICAL DEPARTMENT),
UNIVERSITY OF CAMBRIDGE.

Notes.

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE DETERMINATION OF COBALT IN DRIERS, JAPANS, ALLOYS, ETC.

THE following method is generally useful and time-saving where cobalt is to be determined in the presence of a large number of other metals, as is often the case with the inorganic constituents of varnishes and japans, especially those which have been extracted by organic solvents from the pigment.* The results obtained by the nitroso-beta-naphthol method are as unsatisfactory as those given by Carnot's method (precipitation by means of ammonium molybdate as ammonium cobaltic molybdate). In order to isolate cobalt quantitatively the author succeeded in making the well-known qualitative cobalt test devised by Vogel, quantitative. A solution containing cobalt, nickel, iron, aluminium, chromium, manganese, zinc, tin, lead, copper, titanium, and vanadium was used.

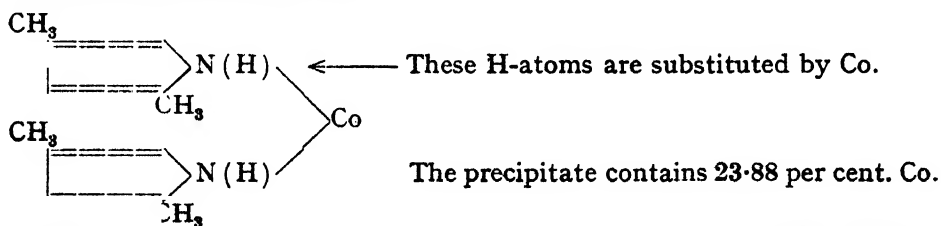
PROCEDURE.—The weak hydrochloric acid solution of the metals is made by treating the ash of the japan, etc., with hydrochloric acid, or, better, by oxidising 10 grms. of the material in a tall beaker or an Erlenmeyer flask by means of about 40 c.c. of sulphuric acid and 20 c.c. of hydrogen peroxide (30 per cent.). After the violent reaction has ceased the excess of water is driven off by boiling until white fumes of sulphuric acid begin to develop. After cooling somewhat, 20 c.c. of hydrogen peroxide are again added, and the mixture treated as before. When the dark liquid has finally become light in colour, indicating the absence of organic matter, the bulk of the sulphuric acid is driven off. After cooling and diluting, ammonia solution and then hydrochloric acid, each in slight excess, are added. If the other metals are also to be determined, the solution is made up in a volumetric flask. To the weak hydrochloric acid solution pure zinc oxide is added at 50° C. in very small quantities until only a visible trace of zinc oxide remains undissolved.† (Even a small excess of zinc oxide will precipitate a little cobalt.) The precipitate is filtered off, and washed with warm water. (It may contain

* In this case there are sometimes quite appreciable amounts of metals (which originally belong to the pigment) extracted in the form of their soaps.

iron aluminium, chromium, copper, vanadium, titanium (and lead, partly).) If properly treated with zinc oxide the precipitate should give a negative "Vogel" reaction for cobalt, which is sensitive to 0.00002 grm. The filtrate may contain cobalt, nickel, manganese, and some of the lead. It is concentrated to a volume of about 20 c.c. and transferred, with several portions of water, quantitatively, to a separating funnel, so that the total volume is not more than 50 c.c. About 30 grms. of ammonium thiocyanate are added and dissolved.

The solution is shaken out with a mixture of ether and amyl alcohol (9:1) until exhausted.† (A Rothe extractor serves better.) The ethereal solution is shaken with 15 to 20 c.c. of dilute (10 per cent.) sulphuric acid and washed several times with water. The excess of water is evaporated from the aqueous solution, and the remainder is neutralised with ammonia and then electrolysed. Or the solution is made alkaline, while hot, with sodium hydroxide, and the precipitate is filtered off, washed very thoroughly with boiling water, ashed and weighed as cobalt oxide.

It is also possible to determine the cobalt, since it is the only metal in solution, by means of its 3, 5-dimethyl-pyrazol compound, as shown recently in the Siemens Laboratory in Berlin. A 2 per cent. solution of this specific cobalt reagent is poured (cold) into the cobalt solution which has previously been rendered nearly neutral with sodium hydroxide. It should still be faintly acid. Then about 5 c.c. of 0.5 N sodium hydroxide solution are added, whereupon all the cobalt settles out as a beautiful purple precipitate, which is analogous to nickel dimethylglyoxime. It is filtered off, washed with cold water, and dried in a Gooch crucible at as low a temperature as possible.



NEW YORK.

OSCAR HEIM.

† If no Fe is present, add a few drops of 10 per cent. FeCl_3 solution.

‡ This is indicated by the disappearance of the blue colour of the ammonium cobaltous thiocyanate.

Notes from the Reports of Public Analysts.

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

COUNTY OF LANCASTER.

ANNUAL REPORT OF THE COUNTY ANALYST FOR THE YEAR 1928.

DURING the year the total number of samples examined was 5395, of which 4933 were Food and Drugs samples (146, or 3.0 per cent. adulterated).

INFORMAL SAMPLES.—There appears to be an idea in the minds of some that "Informal" samples need less care and trouble bestowed upon their analyses than "Formal" samples. Indeed, a memorandum sent out by the Local Government Board in 1914 contained the following words: "The Board understands that, with a view to preliminary investigation 'Informal' samples have been collected in some districts for examination, by rough sorting methods only, by the Public Analyst or by some other person." It is difficult to see how "the use of rough sorting methods . . . by some other person" can have the slightest advantage to anyone. The days have long gone by when the application of rough sorting methods is sufficient to detect adulteration. Even if the use of rough sorting methods is sometimes permissible in the hands of experienced persons, it is obviously highly improper for there to be the slightest possibility of their being undertaken by persons without knowledge, ability or experience.

MILK.—Of the 2771 samples examined, 95 (3·4 per cent.) were returned as adulterated. This figure is much less than that for the whole of England and Wales, which was 6·9 per cent. in 1927, and is very good as compared with the majority of other areas. It should be pointed out, however, that the public analysts for some areas describe as adulterated any sample of milk of which the percentage of solids-not-fat falls below 8·5 per cent. or the percentage of fat below 3·0 per cent., no matter how small the deficiency may be. Other public analysts ignore deficiencies of less than 0·1 per cent., whilst others do not report against a sample unless it is at least 0·2 per cent. below the limit laid down.

Sound arguments can be brought forward for all these methods of treatment; in fact, it does not seem possible to lay down any hard and fast rule, as special circumstances may affect any one particular sample.

"APPEAL TO COW" SAMPLES.—As was pointed out in the Report for 1927, the figures as to the percentage adulteration of milk will not agree with those given in the Annual Report of the Ministry of Health, owing to the fact that the Ministry include "Appeal to cow" samples whose composition is below the minimum limits, whilst they are not included here. In their own Memorandum the Ministry have asked that "Appeal to cow" samples should be excluded from the main tabular statement, and that only such "Appeal to cow" samples as are taken under the provisions of the Milk and Dairies (Consolidation) Act, 1915, should be so included.

It is difficult to see, however, how any "Appeal to cow" sample, if properly taken and properly supervised, can be classed as adulterated. No matter how improper many think it to be, it is undoubtedly quite legal to sell milk below the limits laid down by the Sale of Milk Regulations, 1901, provided that the milk is in exactly the same condition as it was when it came from the cow. If, therefore, it is permissible to describe as adulterated an "Appeal to cow" sample which is below the limits, we are forced into the anomalous position that it is legal to sell an adulterated article.

It is surely better on all grounds to continue along the lines originally suggested by the Ministry.

AVERAGE COMPOSITION OF MILK.—The average fat content of the whole of the milks examined, including "Appeal to the cow" samples, was 3·74 per cent., whilst the solids-not-fat showed 8·90 per cent. The average composition of the milks examined from 1916 to 1928 was: Fat, 3·68 per cent.; solids-not-fat, 8·93 per cent.

The following table shows the average composition of all milk samples in some other districts:

District.	Years.	No. of samples.	Fat per cent.	Solids-not-fat per cent.
Birmingham City	1923-1926	10,215	3.64	8.74
Bolton C.B. ..	1920-1926	1,483	3.61	8.87
Durham County	1917-1926	4,078	3.61	8.64
Hull City ..	1923-1927	2,461	3.70	8.78
Lancaster County	1913-1928	45,370	3.67	8.91
Liverpool City ..	1923-1926	15,375	3.60	8.83
Salford City ..	1915-1925	8,437	3.62	8.85
Stepney Borough	1924-1927	3,400	3.67	8.70
*Somerset ..	1924-1927	36,985	3.72	8.87
*Dorset	1924-1927	51,623	3.74	8.88

* These figures have been obtained from the Laboratory of the West Surrey General Dairy Co. Ltd., and have been supplied by the courtesy of their chief chemist, Mr. J. Tavroges.

Taking the whole of the samples in the above table, which amount to 179,427, the total average is 3.69 per cent. of fat and 8.86 per cent. of solids-not-fat.

Although the average amount of fat in these samples is thus well above the 3.0 per cent. limit, it has been claimed on many occasions that the percentage of fat is seriously diminished during the season when the cows are first put out to grass, diminished so seriously, in fact, that a considerable number, if not the majority of herds, will be giving milk containing less than 3 per cent. of fat.

This is not borne out by a consideration of the average composition of milks for each month from 1913 to 1928 in the County of Lancaster. These figures show that whilst the average percentage of fat for the whole period is 3.67, the total monthly variation ranges from 3.55 to 3.86 per cent. These figures are very similar to those obtained in Somerset, Dorset, Durham, and Salford, and to Richmond's figures.

It may be argued that natural milks of poor quality are very common, and that average figures therefore mean very little, but those who have any experience of milk statistics know that the percentage of herds giving mixed milk below the limits of the milk regulations is quite small.

An analysis of the figures of the milks supplied by 25,000 herds in the County of Lancaster over a period of 9 years has shown that less than 1 per cent. have given milks of lower quality than 3.0 per cent. of fat, and 8.5 per cent. of solids-not-fat. Even those "Appeal to cow" samples which were actually deficient were, as a general rule, only slightly deficient, in many cases so slightly deficient that no Public Analyst would dream of issuing a certificate for prosecution.

In view of these figures and these facts, it is difficult to fix at its true value the following sentence which has lately appeared in a Scottish journal: "... we have an unending succession of scandalous milk prosecutions." It is difficult, if not impossible, to put into official form in a report of this kind the impression that one gets of the methods of those who use this kind of language, but it should be remembered that miscarriages of justice are not always on the side of convictions.

The evidence is available for all those who wish to come to an unbiased conclusion on the whole matter. In view, however, of the repeated publicity of such statements, it may be desirable to indicate the methods which are adopted by the County Council of Lancaster, to avoid, as far as is humanly possible, any miscarriage of justice. When a sample of milk is found to be deficient either in fat or in solids-not-fat, an "Appeal to cow" sample is immediately taken. Every effort is made to take this within 48 hours, although sometimes, on account of distance,

this time has to be somewhat exceeded, but in all cases every reasonable effort is made to have the sample taken as soon as possible. When the results of the "Appeal to cow" sample have been obtained, they are carefully compared with those of the original sample. Where the "Appeal to cow" sample is of approximately the same composition as the original sample, no prosecution is instituted.

In order that a genuine milk considerably below the limits of 3.0 per cent. for fat or 8.5 per cent. for solids-not-fat shall be unjustly accused of being tampered with, two unlikely things must happen at the same time. These two improbabilities are, firstly, that a genuine milk shall have a composition below the legal limits; and, secondly, that having this composition it shall improve so considerably in two days as to suggest that it is not the same milk. It must also be remembered that for a realisation of these unlikely happenings to be a means of embarrassment to the defence they must take place on the very days that the samples are being taken for the prosecution. The possibility of two unlikely happenings occurring in the correct order on two particular days is somewhat remote.

Proceedings may be instituted on any sample the composition of which is below that of the Sale of Milk Regulations, but in practice such proceedings are only commenced when there is certainly a very strong case to answer. Even in these circumstances, however, the defence have their opportunity, and magistrates are quite rightly inclined to the side of the defendant until they are assured that he is guilty.

PEARL BARLEY.—A sample was coated with 0.2 per cent. of mineral facing. Whatever opinions may be held as to the desirability of treating rice in this way, it must be held to be objectionable in the case of pearl barley, which is used in considerable quantities in the preparation of barley water for invalids. The vendor was cautioned.

CREAM CAKES.—Eleven samples contained "cream" composed of an emulsion of margarine and sugar, but no legal proceedings were instituted, as it is desired to arrive at some conclusion as to the nature of the article which a purchaser of a "cream cake" is entitled to expect. In my opinion the expression is not a generic term synonymous with "fancy cake," but is a descriptive term showing that cream enters into the composition of the article.

MAGNESIA.—A sample of magnesia was found to consist of magnesium carbonate. In the British Pharmacopoeia the term "Magnesia" is applied to magnesium oxide, but there is some evidence that the term is popularly applied to the carbonate. Thus the B.P. Codex states: "It was the practice to refer to the carbonates as magnesia and the oxides as calcined magnesia. The practice when 'magnesia' is asked for is not uniform. In the majority of cases what is intended and supplied is the light carbonate." In these circumstances the sample was passed as genuine, but a state of affairs in which either of two substances may be supplied under the same name is obviously most undesirable, and some definite official ruling is required.

G. D. ELSDON.

Legal Notes.

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

CAFFEINE-FREE COFFEE.

On April 24, a trading company was summoned at Bow Street Police Court for applying to coffee a false trade description, and a retail tradesman was summoned for selling the coffee. The label on the tin stated: "P.R. Coffee. Practically caffeine-free, 100 ounces (representing 100 parts of liquid) containing 1-100th part of an ounce of caffeine."

According to the prosecution the P.R. ("physical regeneration") coffee contained 3.37 to 3.7 grains of caffeine per ounce, or more than one hundred times that given on the label.

Mr. J. K. Colwell, Public Analyst for Holborn, said that the amount of caffeine in the coffee, viz. 1.02 per cent., was rather below the average (1.2 per cent.), but there was nothing to suggest that it was not pure coffee, except the statement on the label.

Counsel for the second defendant (the retailer) argued that his client had no reason to suspect that there was anything wrong with "P.R." coffee, and he relied on the warranty of the first defendant.

To this, counsel for the prosecution (Mr. Wishart) replied that a warranty was no protection under the Merchandise Marks Act. The retailer should have procured a certificate of analysis from the wholesaler or have had the coffee analysed himself; otherwise he should not sell goods under a trade description. However, he did not press the case against the retailer, and would be satisfied if the summons were dismissed on payment of costs.

At the adjourned hearing, on May 8, the Magistrate (Mr. Graham Campbell) dismissed the summons against the retailer, without costs, and agreed to an adjournment for the completion of analysis for the defence in the case of the other defendant.

On June 12, evidence was given by Mr. J. B. Coppock that free caffeine might have been found in the coffee, but that the analyst would have to obtain it from caffeine chlorogenate, the properties of which were entirely different from those of ordinary caffeine salts.

The Magistrate said that he was not satisfied that the prosecution had made out their case. The statement on the tins was that the coffee was pale roasted, and was shown by analysis to be practically caffeine-free. The defence contended that this meant that the word "caffeine" must be taken to mean "free caffeine," and not caffeine in combination with other substances. The evidence of the analysts for the prosecution showed that in order to obtain free caffeine they had had to break down the compound. There was always more free caffeine in dark roasted coffee than in pale roasted coffee, so that it was correct to say that there was less caffeine in the coffee in question than in most other kinds. The summons would be dismissed, but without costs, since the nature of the defence was not disclosed until after several adjournments.

OBLITERATING ORIGIN MARKS FROM EGGS.

ON May 16 three tradesmen were summoned at Brighton for removing or obliterating an indication of origin on certain eggs, contrary to the Merchandise Marks Act, 1906.

Evidence was given by an inspector that, on visiting the warehouse of one of the defendants, he saw a crate containing several hundreds of imported eggs bearing the importation mark of Belgium printed in blue. Near the crate were two pails, one containing water and the other water to which commercial sulphuric acid had been added. One of the defendants was taking eggs from the crate of marked eggs and washing them in the pail containing sulphuric acid, from which they were transferred to the bucket of clean water, near which another of the defendants was standing, so that he could take the washed eggs out and dry them. At the back was a crate containing unmarked English eggs, and another box containing eggs similar to those which had just been washed.

The solicitor for the defence submitted that his clients were fairly entitled to the presumption that the marks on the eggs were washed off accidentally and would have been replaced.

The Magistrates found that there was insufficient evidence against one of the defendants, and dismissed the case against him. The other defendants were fined £5 and £2 respectively.

TINCTURE OF IODINE AND SOLUTION OF IODINE.

ON June 13, a trading company was summoned at Ealing Petty Sessions for having sold at their Uxbridge branch a compounded drug, tincture of iodine, not composed of ingredients in accordance with the demand of the purchaser.

Mr. R. A. Robinson, chief officer, Public Control Department, Middlesex County Council, stated that the defendants had exhibited on the counter of their shop cartons labelled "Tincture of Iodine, B.P." and also a full half-bottle similarly labelled. An inspector pointed to the cartons, and asked for tincture of iodine. What should have been supplied was weak tincture of iodine, B.P., containing 2.5 per cent. of free iodine and 2.5 per cent. of potassium iodide, with a trace of water, in 90 per cent. rectified spirit. What was sold was a solution containing only 0.66 per cent. of free iodine in isopropyl alcohol, and no potassium iodide—a cheap substitute for the official tincture. The cartons and bottles containing this article were of the same size and appearance as those containing the genuine tincture, except that the label bore the word "iodine" in large letters and the word "solution" in small letters, instead of the words "tincture of iodine, B.P."

There were several High Court cases establishing the authority of the B.P.; here it gave not only the formula, but also an official test for the amount of iodine. The cost of the genuine tincture was about 8s. per pint, and that of the substituted article between 2s. 6d. and 3s. 3d., according to the percentage strength of the iso-propyl alcohol. This alcohol was regarded as not fit to drink, and was therefore non-excisable. The manager of the shop had told the inspector that he did not know that there was any difference between the two articles, and did not know why the labels were dissimilar. An official drug should not be of one strength one day, and a quarter of that strength on another day, or on the same day.

Mr. F. J. Dyer, B.Sc., A.I.C., said that a pharmacist would always sell Tinct. Iodi. Mit., B.P., when asked for tincture of iodine, or even for a "bottle of iodine." There was no official recognition of such a preparation in any official pharmacopoeia

—nor of any tincture weaker than Tr. Iodi. Mit., B.P. Free iodine was the most important constituent. Potassium iodide was also necessary to keep the iodine in a free state. Combined iodine would not be efficacious.

In cross-examination, the witness agreed that "Martindale's Extra Pharmacopoeia" recommended a solution of iodine in isopropyl alcohol; also that the use of such a solution containing 1.25 per cent. of iodine was recommended in *The Lancet* (1928, Sept. 1, p. 443) as "an external antiseptic for hospital use." Re-examined, he said that "Martindale's Extra Pharmacopoeia" was in no sense an official book, nor had it statutory authority. The *Lancet* article only recommended the solution for external skin asepsis.

Mr. G. Beyfus, for the defence, said that his clients had by accident committed a technical offence. Last year they had sold the B.P. tincture, but in August the Customs and Excise Department raised the question that the tincture should not be sold without a spirit licence. In consequence, they had substituted a 1.25 per cent. solution of iodine in isopropyl alcohol, as recommended in the *Lancet* article. In February communications were received from the Birmingham Health Department, by whom it had been found that the preparation lost strength on keeping. To prevent this, potassium iodide was added. The isopropyl alcohol used was of 90 per cent., instead of 70 per cent. strength as recommended in the *Lancet*. His clients made virtually no extra profit—only one-twelfth of a penny per bottle. It was an unfortunate accident that all of the original bottles had not been disposed of before April.

A representative of the manufacturers said that he had advised the defendants to use the isopropyl solution, owing to the objection of the Excise authorities to their selling the tincture. The defendants had been charged 3s. 6d. per dozen half-ounce bottles of the tincture, and 3s. 5d. for the same quantity of the solution.

Dr. H. E. Cox, F.I.C., said that he had analysed part of the official sample, and had found it to contain 0.67 per cent. of free iodine and also 0.53 per cent. of combined iodine. The compounds formed would include a small percentage of hydriodic acid, and probably some di-iodo-isopropyl compound.

The Bench said that they considered that the defendants had been negligent, but not deliberately fraudulent. They imposed a fine of 40s., with 10 guineas costs.

Department of Scientific and Industrial Research.

FUEL RESEARCH. Technical Paper No. 22.

THE REACTIVITY OF COKE (2).*

THE method used for determining the reactivity of the cokes is based on the reaction $\text{CO}_2 + \text{C} = 2\text{CO}$, the value recorded being the volume of carbon monoxide obtained from 100 ml. of carbon dioxide under standard conditions. The standard volume of coke is heated to 950° C. during 1 hour in a stream of nitrogen passing at the rate of 1 litre per hour. Conditions are then kept constant for one hour, and then 100 ml. of carbon dioxide are passed over the coke at a prescribed rate. The actual determination is then begun by passing another 100 ml. of carbon

* *Examination of a Number of Metallurgical Cokes*, by J. H. Jones, J. G. King and F. S. Sinnatt. Obtainable at Adastral House, Kingsway, W.C.2. Price 1s. 0d. net.

dioxide over the coke and collecting the gases over a solution of potassium hydroxide. The volume in ml. of insoluble gases collected is Reactivity I, and is the closest approximation to the primary reactivity value of the coke that can be obtained under experimental conditions. When carbon dioxide is passed over coke kept at 950° C. the volume of carbon monoxide obtained from 100 ml. alters until such a condition is established that the volume obtained in successive determinations is practically constant. This is Reactivity III. Results were obtained for 78 cokes prepared from a variety of coals in different types of ovens, and these show that the cokes may be broadly classified by their reactivities according to the fields whence they were obtained. Shatter* indices obtained for 50 of the cokes show that there is a rough agreement between these and the reactivity values, in that the higher the reactivity value the lower the resistance to shatter, but the relationship breaks down when extended to particular cases. So far there is little accurate information as to comparative behaviour of cokes in the blast furnace, so that at present it can only be said that the results of the investigation indicate that low reactivity is desirable, but that regularity of behaviour may be of greater importance. The effect of the ash on the reactivity of metallurgical cokes is being investigated, and the removal of certain inorganic constituents has already been found to influence the Reactivity I value. For example, the gradual removal of iron caused a gradual fall in Reactivity I.

D. G. H.

* The Shatter indices were determined at the Fuel Research Station or at the laboratories of the Coke Research Committees, or were given by private companies. In all cases the index was recorded as the percentage of coke remaining on a 2-in. sieve after the test.

Ministry of Agriculture and Fisheries.

"VARIATIONS IN THE COMPOSITION OF MILK."

THE Committee of Public Analysts of the Society of Public Analysis has sent the following letter to the Ministry:—

SIR,

The Committee of Public Analysts of the above Society has had under consideration Miscellaneous Publication No. 65, recently issued by the Ministry of Agriculture and Fisheries, and entitled "Variations in the Composition of Milk."

The Committee is of opinion that the publication has the effect of giving a wrong impression of the composition of milk as produced in this country. Although the object of the publication may not be to undermine the Sale of Milk Regulations, 1901, and to question the validity of the principle of the "appeal to cow," it cannot but tend to have this effect.

We make the following criticism of the data included in the publication and of the conclusions which might be drawn from them:—

We consider that although milk as drawn from the cow does at times fall below the limits contained in the Sale of Milk Regulations, the frequency of this occurrence is exaggerated. For instance, the table contained on page 4 would tend to indicate that 10 per cent. of the samples obtained from herds of cows in

this country would fall below 8.5 per cent. of solids-not-fat, and about 7 per cent. below 3 per cent. of fat. The statement at the foot of page 4 that this impression is not intended loses weight in view of the data quoted on page 5.

During last year, out of 63,000 samples of milk taken under the provisions of the Sale of Foods and Drugs Acts only 6.9 per cent. were returned as being not genuine, but these include not only samples watered or separated, but also those containing preservatives, dirt or added colouring matter. It is obvious that the proportion of naturally deficient samples must fall well below 6.9 per cent. In this connection the results published by Liversidge (*ANALYST*, 1926, 51, p. 295) may be considered. They show that during 21 years 216 farms were visited, all of which had been sending deficient milk to Birmingham. Of the 434 samples taken at these farms 20 per cent. were found to be deficient in solids-not-fat, and 3 per cent. to be deficient in fat. This suggests that only about one-fifth of the samples originally found to be deficient were so naturally, and about four-fifths either deliberately adulterated or deficient owing to improper milking or subsequent careless handling, etc. If this proportion were to hold with regard to the 63,000 samples quoted above, the percentage of samples deficient in one respect or the other from natural causes would only amount to 1.4 per cent. This figure is confirmed by results obtained elsewhere.

Allowance must also be made in public analysts' returns for the fact that the apparent percentage of adulteration is increased through the taking of more than one sample from the same source when milk has been found to be unsatisfactory.

There is nothing to warrant the assumption that between 7 and 8 per cent. of the milk churns delivered to Dairies A and B (see page 5) and found to be deficient in fat, or 5 per cent. low in solids-not-fat, were in fact naturally poor, and had not been adulterated. We are, therefore, of opinion that it would not be right to put forward the high proportion of deficient milks generally quoted in the report as truly representing the produce of herds in this country.

Prominence is given in the publication to milk of individual cows. On page 6, extreme examples are given, and the publication proceeds to say that "it is clear that the presence in mixed milk of any considerable proportion of milk of cows, such as this, will affect the quality of the mixed milk." It is unlikely that a considerable proportion of *extreme* cases would occur in one herd. The quality of milk given by an individual cow, especially when it represents an extreme example, so frequently quoted in the publication, is of no use when judging the average quality of milk yielded by a herd.

In the publication, as a rule, milks are classed as deficient, no matter how small the deficiency may have been. Very small deficiencies have but a slight bearing upon the validity of the Sale of Milk Regulations, as no prosecution would probably be instituted in such cases, though the Annual Report of the Local Government Board, 1911-12, contains the following instruction:—"Whether it is considered that legal proceedings should or should not be instituted in the case of apparently slight adulteration, it remains the duty of the analyst to class as "adulterated or not up to standard" all milk samples failing to reach the minimum limits fixed by the Regulations."

The publication invariably mentions solids-not-fat as an entity, and gives no indication that the composition of the solids-not-fat has received attention. We are confident that a more complete analysis of the solids-not-fat, at any rate in the more highly deficient milks, would have disclosed such abnormality that the presence of added water would not have been indicated.

The matter of day-to-day variation in the composition of milk becomes of great importance in connection with "appeal to cow" samples. On this question the publication is unsatisfying in the extreme. Two graphs are given showing

the variation in the case of single cows; for practical purposes these may be neglected. One graph showing the daily variation of the milk of one herd is quoted, but as all the figures given for solids-not-fat are above 8·5 per cent., with the exception of one (*viz.* 8·46), and all the figures are above 3 per cent. for fat, this graph has no bearing on the issue for which "appeal to cow" samples are taken. Yet, on page 18, the very wide conclusion is drawn that ordinary market milk may be expected to show even larger variations than 0·87 per cent. of solids-not-fat between one milking and the next, without any mention of the fact that all the results on which the conclusion is based were, as already stated, higher than the minimal limits. The publication may be held to record the conclusion of the Ministry that the measure which enables a vendor to have samples taken from the cow is of no utility, and with this we do not agree.

We feel that the efforts of the Ministry should be directed to encouraging farmers to produce a high quality of milk, rather than to render the position of the producer of good milk more difficult, and the more so because we realise the danger of developing strains of cows giving quantity of milk without any regard to quality.

The Committee considers the publication of Miscellaneous Publication No. 65 as unfortunate and inopportune. It gives prominence to the composition of exceptionally poor milk and thereby not merely throws doubt upon the adequacy of the present standards adopted for genuine milk, but may even encourage the production of milk of low quality. As the publication will, no doubt, be made use of in courts of law, the punishment of adulteration will be rendered more uncertain. The fact has not been considered that a public analyst does not merely determine the amounts of solids-not-fat in a low or doubtful milk, but he also determines the composition of the solids-not-fat, and this analysis weighs with him before reporting as to the genuineness or otherwise of a sample.

Though we are not, at the moment, in a position to challenge the accuracy of the published results, or the conditions under which the samples were taken, we think that in a document, such as this, bearing an inferred endorsement by the Ministry, the analytical results should in all cases have been conducted and vouched for by analysts of repute.

We are, sir, your obedient servants,

(Signed) E. HINKS (Chairman).

F. W. F. ARNAUD (Hon. Sec.)

United Provinces of Agra and Oudh and Central Provinces.

ANNUAL REPORT OF THE CHEMICAL EXAMINER FOR THE YEAR 1928.

THE Chemical Examiner (Mr. D. N. Chatterji) reports that 1797 cases were investigated during the year, as compared with 1573 in 1927. Of these, 1597 were medico-legal cases (1402 in 1927). Inspected human poisoning cases showed an increase from 468 to 509; cattle poisoning cases increased from 33 to 53; and stain cases from 881 to 1014.

POISONING CASES.—Poison was detected in 311 of the 1114 articles examined. The favourite poisons were arsenic (133 articles), opium (35), datura (74), copper sulphate (10); strychnine (7), potassium cyanide (4); mercury (7).

In the cattle poisoning cases arsenic was found in 29 cases, opium in 2, bhang (Indian hemp), yellow sulphide of arsenic, and mercury in 1 case each.

GHEE.—Forty-three samples were examined, as against 12 in the previous year. All except 9 were adulterated with animal or vegetable fats or with sesame oil.

Siam.

REPORT OF THE GOVERNMENT LABORATORY.

THE Director of the Government Laboratory of Siam (Mr. A. Marcan, F.I.C.), in his 4th Report to the Ministry of Commerce and Communications, covers the period from April 1st, 1926, to March 31st, 1928.

The analysis of opium dross is the only branch of the work which may be designated as repetition work, and even here it is of interest to note that some adulterated drosses defy the usual methods of morphine determination, owing to the addition of a protective colloid.

Reports on materials of interest included the following:—

HYDNOCARPUS ILICIFOLIA OIL.—The trees grow extensively in Siam. A sample of the dried kernels yielded 36.1 per cent. of crude oil on extraction with ether. Two samples of cold-pressed oil gave the following values: Acidity (as oleic acid), 21.0 and 0.6 per cent.; sp. gr. at 30°/4° C., 0.944 and 0.947; saponification value, 203.6 and 213.1; iodine value (Wijs), 89.7 and 89.7; specific rotation, $[\alpha]_D^{20}$, 52.7 and 51.2; n_D^{20} , 1.4739 and 1.4763; m.pt. 25.8° to 32.6° C., and 23.0° to 28.2° C. The oils and the esters prepared from them were very similar to those from *Hydnocarpus anthelmintica*. Clinical tests are in progress in the Leprosy Research Laboratory, Calcutta.

KRATOM EATING.—Kratom leaves from *Mitragyne speciosa* are much used for chewing in Peninsular Siam and, to a small extent, in Bangkok. Investigations of the physiological action of the alkaloid, mitragynine, are still in progress. According to the reports of the officials of the Revenue Department the chewing of kratom leaves is habit-forming. Addicts appear to be able to endure great fatigue and exposure to heat. The habit has not a bad reputation, like opium smoking, nor does there seem to be any progressive change in the condition of the addict or in his character. On the other hand, educated people avoid the habit. Habitual eaters are thin, having unhealthy complexions and dark lips. No immunity from malaria is conferred. A fresh leaf weighs on the average 1.7 grms., and 0.43 grm. when dry, and contains about 0.2 per cent. of mitragynine; other alkaloids appear to be present. When an excess of the leaves is eaten vomiting and dizziness are produced; numbness of the body, twitching of the hands and feet, and an effect on the heart have also been reported. From 10 to 30 leaves are usually taken from 3 to 10 times a day, and water is drunk after chewing.

CURCAS OIL.—Oil extracted from the seeds of *Jatropha curcas*, which is grown as a hedge plant in Siam, gave the following values: Sp. gr. at 15.5° C., 0.923; n_D^{20} , 1.4623; saponification value, 202.9; iodine value (Wijs), 98.2; and acidity

(as oleic acid), 12.4 per cent. The oil is thus similar to the commercial oil from other countries, except that it has a high acidity.

TOXICOLOGICAL EXAMINATIONS.—Fifty-four exhibits (representing 33 cases) were examined for poisons, and 26 of these were found to contain them (16 cases). Arsenic was found in 16 articles, apomorphine in 1 viscera, atropine in 1 drug, calomel in 1 horse dope, copper in 1 viscera, morphine in 1 drug, and strychnine in 1 drug and 1 viscera.

A poisonous fish, identified as a species of *Tetraodon* (globe fish) was a new-comer in the list of poisons. In one case a soldier died 3 hours after eating the fish. In another case the gall bladder of the fish was mixed with the juice of *Excoecaria agallocha*, and a *Croton tiglium* seed, and added to water. Two children died, and two adults recovered. It is reported that in Kelantan the gall bladder of a species of *Tetraodon* is used as a poison, and is frequently mixed with Upas Sap or intestinal irritants.

Some of the above cases may well make the toxicologist in the tropics ponder as to how far and how often the criminal is ahead of him. A glance at such a work as Gimlette's "Malay Poisons and Charm Cures" will show that many poisons are in use which find no place in systematic toxicology. In the East the criminal has all the resources of the jungle at his disposal, including many plants of which the active principles have not been investigated. In the West, the poisoner, as a rule, has to depend on what refined active drugs he can purchase, which limits his powers for evil to a great extent. The situation is worthy of consideration by those with time and facilities at their disposal for toxicological research.

DEPARTMENT OF PUBLIC HEALTH.—Pickled shellfish (apparently mussels) submitted as causing illness, were examined for arsenic, as mussels in Europe have been found to contain up to 119 parts of arsenious oxide per million. This exhibit only contained 0.5 part of arsenic (As_2O_3) per million.

Chenopodium Oil.—A sample of mixed chenopodium oil (2 vols.) and carbon tetrachloride (3 vols.) for hookworm treatment, stored for one year, was submitted for examination for toxicity. The separated carbon tetrachloride was found to conform to the stringent standards of purity for internal use. No hydrolysis of the carbon tetrachloride had taken place, but, as ascaridole decomposes at low temperatures when diluted with volatile indifferent solvents (Henry and Paget, *J. Chem. Soc.*, 119, 1722), it appears preferable to store the two drugs unmixed. Any decomposition of the ascaridole would probably reduce the toxicity of the chenopodium oil, and also its value as an anthelmintic.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Detection of Apple and other Fruit Juices in Wine. J. Werder. (*Ann. Falsif.*, 1929, 22, 260–261.)—Sorbitol is present in Sorb fruits and in nearly all *Rosaceae* fruits, but not in grapes. It combines with 2 volumes of benzaldehyde to form the insoluble amorphous white compound, dibenzal-sorbitol. In order

to detect it, 7 grms. of pure animal charcoal are added to 100 c.c. of the liquor, fermented as completely as possible, and the boiled liquid is filtered hot, placed in a 300 c.c. distilling flask, carrying a capillary tube through its cork, reaching to the bottom of the flask, and closed by rubber tubing and a pinch cock. The side-arm is connected with a vacuum pump, and the solution is concentrated on a water-bath under reduced pressure until it becomes strongly viscous. The vacuum is maintained until room temperature is reached, when 4 drops of benzaldehyde and 1 c.c. of 1:1 sulphuric acid are added, and, after shaking, the flask is left overnight. If 10 per cent. or more of fruit juice are present, the mass will be solid, but with pure wine it will be liquid. Water (100 c.c.) is added, little by little, and with constant shaking, when the insoluble dibenzal-sorbitol will be precipitated as white flakes. The product of pure wine is soluble, although a slight precipitate is sometimes present. If the results are doubtful, the test is repeated with 200–300 c.c. of wine, and the nature of the precipitate determined by Foch's method, whereby the diabenzenal sorbitol is transformed into the easily crystallisable hex-acetylated sorbitol. A blank test should be made with a pure wine of the same district, and also a test made with the wine to which 10 per cent. of cider has been added. (Cf. ANALYST, 1929, 422.)

D. G. H.

Palm Oil from the Belgian Congo. G. S. Jamieson and R. S. McKinney. (*Oil and Fat Ind.*, 1929, 6, 15–17.)—This oil, from Port Maladi, gave the following values: Sp. gr. at 25°/25°, 0.9146; n_D^{20} , 1.4578; acid value, 20.6; saponification value, 197.9; unsaponifiable matter, 0.39 per cent.; iodine value (Hanus), 53.7; acetyl value (Andr -Cook), 15.3; Reichert-Meissl value, 0.10; Polenske value, 0.29; saturated acids (corrected), 44.3 per cent.; unsaturated acids (corrected), 50.6 per cent.; iodine number of unsaturated acids, 99.9. The percentages of the different glycerides present were: Oleic, 47.2; linolic, 5.6; myristic, 0.5; palmitic, 40.8; stearic, 5.2; lignoceric, 0.1. This is the first indication of the presence of lignoceric acid in palm oil.

T. H. P.

Composition of Gum Arabic. C. L. Butler and L. H. Cretcher. (*J. Amer. Chem. Soc.*, 1929, 51, 1519–1525.)—A botanically authentic sample of gum arabic Cordofan from *Acacia Senegal* (L.) Willd. was hydrolysed for 20 hours with 2 per cent. sulphuric acid, and the salt obtained by treatment with calcium carbonate was purified by precipitation with methyl alcohol. Analysis indicated 28.3 per cent. of an aldobionic acid, $C_{12}H_{20}O_{12}$, identical with O'Sullivan's λ -arabinosic acid. This was confirmed by the percentage of carbon dioxide liberated on boiling with 12 per cent. hydrochloric acid, from the calcium content, and from the iodine required for oxidation. By removal of the calcium as oxalate a mixture of aldobionic acid and its lactone was obtained. The sugar constituent of the acid had the rotation of *d*-galactose, and yielded mucic acid on oxidation. Since simultaneous oxidation and hydrolysis of the acid by boiling with hydrobromic acid in the presence of bromine (Goebel, *J. Biol. Chem.*, 1927, 74, 619) produced saccharic acid, it is concluded that the acid is a galactoso-glucuronic acid which retains its uronic acid residue intact after oxidation, the linkage being between

the aldehyde group of the glucuronic acid and a hydroxyl group of the galactose. Such types of compound have hitherto been found only in products of bacterial metabolism. The sugar fraction of the hydrolysis product was shown to contain *d*-galactose (29.5 per cent. of the ash-free arabic acid), *l*-arabinose (34.4 per cent.) and methyl pentose (14.2 per cent. as rhamnose hydrate). Titration of arabic acid in hot and cold solution showed it to exist as lactone to the extent of about 22 per cent., and indicated an equivalent weight of 1030. J. G.

Method of Identification and Determination of the Value of Rhubarbs, based on Fluorescence. Maheu. (*Ann. Chim. Anal.*, 1929, 11, 165-168.)—For some time a new variety of rhubarb from Asia has been in the market, sometimes under the name of "Indian rhubarb." It has been examined under ultra-violet rays to see if it has the properties of true rhubarb or of rhapontic (bastard monk's rhubarb); it gave the rhapontic reactions in most cases. The author has now made a systematic study of the action of ultra-violet rays from a mercury vapour lamp on rhapontics and on rhubarbs, on the drugs themselves, their powders, and on pharmaceutical preparations (tinctures, extracts) which are derived from them. The results show that all true officinal rhubarbs give a velvety brown red fluorescence under ultra-violet light. European rhubarbs are produced by three or four species of *Rheum*: *R. rhaponticum*, *R. undulatum*, *R. emodi*, *R. compactum*. All these species are Asiatic, imported into Europe and cultivated in England, Austria, Russia and France. Of these, *R. emodi* gives a velvety brown red fluorescence, identical with that given by the officinal types; Austrian rhubarb (from *R. undulatum*) gives a deep violet fluorescence, and French rhubarb (from *R. rhaponticum*) gives a very clear violet fluorescence. The powders which correspond to these rhizomes show the same macroscopic signs of fluorescence. Mixtures of powders of rhapontic and of rhubarb show a violet fluorescence, which gets darker as the proportion of rhapontic is decreased; in a mixture which only contains 10 per cent. of rhapontic the colour is still violet. A microscopic fluorescence method is described for the determination of the percentage of rhapontic powder added to a rhubarb powder. The mixture to be analysed is compared with mixtures of known percentages. By this means 1 per cent. of powder of rhizome of rhapontic can be determined in rhubarb powder. The parenchyme cells of false rhubarb appear bright violet under the microscope. Tinctures give the same fluorescence colours as the powders. An alcoholic extract of rhapontic gives a white milky fluorescence, and that of rhubarb gives an orange brown. Rhizomes of rhubarbs, tested with ultra-violet rays, can be divided into:—(1) True rhubarbs: *R. officinale* H. BN.; *R. tanguticum* Wall.; and *R. emodi* Wall., which give a brown fluorescence and can be considered as officinal, and (2) rhubarbs produced by *Rheum compactum* L., *R. undulatum* L., *R. ribes* L., *R. rhaponticum* L., which produce Austrian, English and French rhubarbs which give a violet fluorescence, and must be considered as non-official. In conclusion, all rhubarbs, rhubarb powders, and tinctures which under ultra-violet rays give a violet fluorescence should be rejected. P. H. P.

Reaction for the Ergot of Rye Alkaloids, Ergotamine, Ergotoxine and Ergotinine. Examination and Colorimetric Determination of Rye Alkaloid Preparations. H. W. Van Urk. (*Pharm. Weekblad*, 1929, 66, 473-481.)—The author's *p*-dimethyl amino benzaldehyde reagent (*id.*, 1929, 66, 101) is preferable to the (Dutch) Pharmacopoeia test (Tanret's test) or to the nitro-benzaldehyde reagent (*ANALYST*, 1929, 424) for these alkaloids. A one per cent. alcoholic solution is added to the alkaloid in the presence of 2 per cent. of sulphuric acid in the form of a ring test, or preferably, the violet to red colour may be produced by evaporation on the water-bath of the reaction mixture. Coloured samples, such as tinctures and extracts, are shaken with five times their volume of ammoniacal ether and the ethereal extract used for the test. In this case it is preferable to add directly an ethereal solution of the reagent rather than to use the residue after evaporation. The Pharmacopoeia method is rendered more sensitive by the addition of a trace of oxidising agent, *e.g.* ferric chloride. The method may be adapted to the colorimetric determination of 0.01 c.c. of a 1 per cent. solution of ergotinine, 0.025 c.c. of a 0.1 per cent. solution of ergotoxine, 0.05 c.c. of a 0.005 per cent. solution of ergotamine, 0.125 c.c. of 0.01 per cent. tincture or 0.25 c.c. of 0.05 per cent. extract.

J. G.

Biochemical.

Biochemical Determination of Allantoin in the presence of Urea. R. Fosse, A. Brunil and P. de Graeve. (*Comptes rend.*, 1929, 188, 1418-1420.)—Allantoin is totally transformed into allantoic acid by the enzymes of *Soja hispida* seeds in the presence of ammonium carbonate. A solution of allantoin containing 1 gm. or less per litre is mixed with 1 per cent. of recently crushed soya bean, 1 per cent. of ammonium carbonate solution, and chloroform, and kept at 60° C. for 5-6 hours, or at 40° C. for 10 hours. Five c.c. of the filtered liquids are neutralised in the presence of methyl orange, and hydrochloric acid is added until the solution is 0.05 *N*. This is warmed for 30 minutes at 60° C., made alkaline with sodium hydroxide, and cleared with mercuric iodide in acetic acid. To the filtrate and washings are added twice the volume of acetic acid and one-twentieth of the total volume of methyl xanthidrol. The condensation takes 4 hours. If urea is substituted for the ammonium carbonate the transformation of the allantoin is still complete.

D. G. H.

Biochemical Determination of Allantoin in Urine. R. Fosse, A. Brunel and P. De Graeve. (*Comptes rend.*, 1929, 188, 1632-1634.)—Allantoin may be determined in the presence of urea by the simultaneous action of the enzymes of soya bean followed by hydrochloric acid. Allantoin is first transformed in alkaline reaction into allantoic acid by allantoinase, and urea is destroyed by urease. Hydrochloric acid is then used to destroy the urease and liberate urea (which is weighed as the xanthylated base), and glyoxylic acid. No other substance must be present capable of forming urea under the given conditions,

and uric acid must, therefore, be eliminated by means of Denigès' reagent (acid mercuric sulphate), which is without action on allantoin, but precipitates urea in solutions containing over 1 part of 100,000. The allantoin found per litre in the urine of a rabbit was 1 grm.; and in that of a dog (1) 1.92 and (2) 2.60 grms.

D. G. H.

New Method for the Determination of Urea. F. W. Allen and J. M. Luck. (*J. Biol. Chem.*, 1929, **82**, 693-701.)—The authors have sought to improve the following three features of the method of Luck (*J. Biol. Chem.*, 1928, **79**, 211; *ANALYST*, 1928, **53**, 607) for the determination of urea, which consisted in principle in the oxidation of its xanthidrol derivative with potassium permanganate:—(1) The end-point of the titration (yellow to colourless) is not sufficiently sharp, (2) the sample to be titrated may not exceed 2 mgrms. of the derivative, and (3) the relationship between the permanganate and material oxidised is merely empirical. These undesirable features have now been overcome. A micro method is described for the precipitation of urea as dioxanthidryl urea from urine, blood and animal tissues. The derivative is determined by oxidation with potassium dichromate and sulphuric acid in place of potassium permanganate. The excess of the oxidising agent is determined iodimetrically. For the determination of urea in muscle and other tissues the use of copper sulphate and baryta is recommended for clarification of the tungstic acid extract. No loss of urea results from this procedure, since added urea is quantitatively recovered, urea values are independent of the amount of copper sulphate employed per unit weight of tissue, and the values obtained are identical with those yielded by extracts from two other methods of precipitation and clarification, namely, Tanret's and the phosphotungstic acid method.

P. H. P.

Relations between Constitution and Taste of Pungent Principles. N. A. Lange, H. L. Ebert and L. K. Youse. (*J. Amer. Chem. Soc.*, 1929, **51**, 1911-1914.)—Capsaicin, the pungent principle of cayenne pepper, and piperin or chavicin, the pungent principle of black pepper, are both acid amides; therefore it was thought that a relation might exist between pungency and the amide structure. The synthesis of a number of closely related amides has shown this relation to exist, and has led to conclusions as to the effect on pungency which accompanies changes in the molecular structure. In compounds similar to capsaicin, a free phenolic group (preferably in the para position to the side chain) in the amine portion is necessary to produce pungency, the methoxy group in the meta position exerts a favourable influence toward pungency, the pungency is a maximum when the acid portion consists of nine to ten carbon atoms, and the pungency is not influenced by the position of the double bond in the acid portion. Capsaicin and closely related substances, apart from the pungent taste, are practically devoid of odour or flavour; dulcin, the carbamic amide of phenetidine, is very sweet. It seemed of interest to prepare a series of compounds which would have a close similarity to capsaicin and dulcin. The following six different substituted ureas and thioureas, which are the carbamic or thiocarbamic amides

of vanillylamine, and analogues of capsaicin (a carboxylic amide of the same amine), were therefore prepared and are described:—Vanillylurea, vanillylthiourea, phenylvanillylurea, phenylvanillylthiourea, *p*-tolylvanillylthiourea and *o*-tolylvanillylthiourea. They were tested particularly for their taste. The last three have the property of pungency, but to a lesser degree than capsaicin. None of the compounds has a sweet taste, for the effect of the phenyl and tolyl groups, which are known to repress the sweetness of compounds, predominates over the favourable effect of the methoxy group. The slightly bitter taste which is characteristic of many thioureas was observed in several of these compounds.

P. H. P.

Test for Vitamin A in Margarine, Butter and Other Fatty Foods.

A. Andersen and E. Nightingale. (*J. Soc. Chem. Ind.*, 1929, 48, 139–140 T.)—The vitamin A content of cod-liver oil can be determined by direct colorations with antimonious chloride, but with butters or margarines reliable direct colorations cannot be obtained; cod-liver oil is 30 to 100 times as potent in vitamin A as butter, and with it there is little or no interference from natural pigments or artificial colouring matter. With butters the vitamin A must be concentrated, and the influence of pigments and colouring matters eliminated before the antimonious chloride test can be applied. The authors have devised a comparative test on butters, oils and fats, margarines, etc., which contain vitamin A, which takes advantage of the fact that the vitamin fraction is associated with the extractable unsaponifiable matter. The test, which furnishes a fairly rapid method of analytical control to ascertain the degree to which vitamin A is present, is as follows:—Ten grms. of the sample under examination are weighed into a 300 c.c. flat-bottomed flask, and 4 c.c. of 56 per cent. aqueous potassium hydroxide solution, and 10 c.c. of alcohol are added from pipettes. The flask and contents are heated at 40–50° C. until clarification results, and gently shaken for 5 minutes. The resulting soap solution is cooled to room temperature, and made up to 100 c.c., and 25 c.c. of this soap solution (=2.5 grms. of margarine or butter) are transferred to a separating funnel together with 50 c.c. of methylated ether (sp. gr. 0.720). The funnel is stoppered, the contents thoroughly shaken and allowed to separate, and the soap liquor is run off. The ethereal layer is run into a porcelain beaker (used to exclude transmitted light as far as possible) and the soap liquor is successively extracted in the funnel with 30 c.c., 20 c.c., and two 10 c.c. portions of ether, and all the fractions are collected in the beaker. The combined ethereal extracts, together with a little ether used to rinse the beaker, are poured into a clean separating funnel containing 30 c.c. of cold distilled water, and the aqueous layer is run off without shaking, in order to remove most of the soap contained in the ethereal extract without risk of emulsification. The ethereal solution is then shaken and washed with 4 successive 20 c.c. portions of distilled water, and then left for 5 minutes in contact with 5 to 10 grms. of anhydrous sodium sulphate, with frequent vigorous shaking, after which 0.1 grm. of good alkali-washed decolorising charcoal, such as "norit," is added, and after further shakings the ether is filtered off (funnel and filter paper being washed with ether) into a porcelain

beaker. After distillation, or evaporation on a water-bath, of the ether, the residual unsaponifiable matter is dissolved in 2.5, 5 or 10 c.c. of chloroform, according to the expected strength of the reaction. If still coloured, which is unlikely, 0.1 gm. of charcoal must again be added and the solution filtered. One c.c. of the chloroform solution is mixed with 1 c.c. of antimonious chloride (24 per cent. SbCl_3 in chloroform by weight, dissolved by shaking and not by heating), and the coloration noted; the final test must then be made as soon as possible. A "dilution test" is used for the measurement, *i.e.* the unsaponifiable matter is diluted in chloroform until the blue colour with antimonious chloride is just visible, or on the point of vanishing. If the total unsaponifiable matter from 10 grms. of butter or vitaminised margarine could be made up to 430 c.c. (=1 gm. to 43 c.c.) with chloroform, and 1 c.c. of the resultant solution still gave a just perceptible blue colour with 1 c.c. of reagent, the dilution strength would be 43. An aliquot portion only of the unsaponifiable matter is measured. The following are some characteristic figures obtained:—

Substance.	Dilution figure.
Unsaponifiable matter from cod-liver oil	Up to 1 million.
Medicinal cod-liver oil. Average of 100 market samples (direct dilution of oil)	1950
Butter	25-60
Ordinary vegetable margarine	Nil
Ordinary oleo-margarine	Trace
Viking margarine (vitaminised)	52-65

The accuracy and reliability of the test have been confirmed by duplicate tests by independent laboratories and by biological tests. The method has been applied to "oleo oils," and extended to food products, such as, cakes, bread, eggs, etc. An extension of the method to the assay of milk and certain milk products is in progress.

P. H. P.

Vitamin B Terminology. (*Pharm. J.*, 1929, 122, 451.)—A Committee of the American Society of Biological Chemists has reported as follows:—(1) That the term "Bios" should be used to designate the factor or factors encouraging the rapid growth of yeast cells; (2) That the term "B" should be restricted to the more heat-labile (anti-neuritic) factor; (3) that the term "G" should be used, for the more heat-stable, water-soluble dietary factor, called the "P-P" (pellagra-preventive) factor by Goldberger and his associates. (4) That the naming of newly discovered dietary factors by other than descriptive terms should be discouraged until their identity has been established beyond doubt. It is suggested that American, British and Continental Committees should co-operate in settling questions of vitamin terminology.

Further Progress towards the Isolation of the Antineuritic Vitamin (Vitamin B) from Brewers' Yeast. A. Seidell. (*J. Biol. Chem.*, 1929, 82, 633-640.)—The antineuritic concentrate previously prepared by Seidell (*J. Biol.*

Chem., 1926, 67, 593) has now been further purified by benzylation in alkaline solution and extraction with chloroform. The aqueous solution thus formed was found to contain only about one-fourth of the nitrogen originally present in the concentrate, and also the major part of the antineuritic vitamin. This highly active aqueous solution, when poured into 10 volumes of acetone, yields a nearly white precipitate of salts which contains less than one-half of the remaining nitrogen (about 0.25 per cent.), and again most of the antineuritic vitamin. The final nitrogenous product protects pigeons from loss in weight on a diet of polished rice in doses of about 60 mgrms., *i.e.* doses which contain 0.15 mgrm. of nitrogen. The quantity of each sample required to protect varied inversely with the percentage of nitrogen which it contained. Therefore it appears most probable that the activity lies in the nitrogenous compound present, but there is as yet no indisputable proof of this point. Judged on the basis of nitrogen activity, the final product represents a purification of antineuritic material more than 100 times that of dried brewers' yeast. A very careful study will be necessary to develop a method for the final separation of the active from the inactive components of the mixture.

P. H. P.

Effect of Drying and of Sulphur Dioxide upon the Antiscorbutic Property of Fruits. A. F. Morgan and A. Field. (*J. Biol. Chem.*, 1929, 82, 579-586.)—The effect of various methods of preservation upon the vitamin C content of foods is of great importance. Inconsistent results by previous workers are discussed. The more acid foods, such as citrus fruits and tomatoes, contain more of the antiscorbutic vitamin than others, and are also better able to resist destruction by drying or processing. Experiments are now described in which peaches of known origin, namely, fresh, sun-dried and dehydrated, both sulphured and unsulphured, have been tested on guinea pigs for vitamin C content. The sulphured peach products retained the full antiscorbutic vitamin content of the fresh fruit, but the unsulphured sun-dried and dehydrated peaches retained no detectable amount of this property. In view of the long-disputed question as to the possibly deleterious effects of sulphurous acid in dried fruits, these results are somewhat surprising. The objection to excessive sulphuring seems to be on the score of the possible marketing of excessively watery dried fruits, rather than based on the danger of physiological injury resulting from their ingestion. Data already obtained upon prunes and apricots, which substantiate these conclusions, will be published later. The suggested possible relation of vitamin C protection to a minimum sulphur dioxide content or acidity is now under investigation. The sulphured dried peach preparations were found to rank with orange juice, raw tomatoes, and other highly potent antiscorbutic foods; 1 gm. daily of the sulphured dried peaches protected standard guinea-pigs from scurvy over a period of at least 90 days; for similar protection 1.5 to 3 grms. of oranges or lemon juice, or fresh tomato, 3 times as much banana, 6 times as much raw apple or pear or cooked potato, and nearly twice as much pineapple are required. The minimum protective dose of fresh peaches is given as 8 grms. daily.

P. H. P.

Bacteriological.

Penetration of Ultra-violet Rays through Fabrics. A. Latzke. (*Amer. J. Hyg.*, 1929, 9, 629-645.)—Measurements of the protective action of various black and white fabrics on bacteria (*B. coli*) when light rays are allowed to penetrate the fabrics and when the rays exert their action on fabrics inoculated with the organisms, indicate that bacteria are held in a fabric by some physical force which renders difficult the removal of a large proportion by the mechanical process of washing. Exposure for 10 minutes to ultra-violet rays is more effective in its germicidal action to organisms on white cotton, linen and silk than to those on a woollen fabric of similar percentage interspace, and the action is less with black than with white material.

When the fabric is used merely as a screen for light rays, and the time of exposure is uniform, black offers greater protection to bacteria than white material. Light seems to be more effective in destroying bacteria through silk and linen than through cotton and wool. When the duration of the exposure was varied according to ratios established with sensitised paper, and the bacteria screened by black fabric were given an exposure three times as protracted as with white fabrics, the light passing the black fabrics proved the more highly bactericidal. Hence the size of interspace appears more important in the transmission of ultra-violet rays of germicidal properties than the colour of the fabric.

T. H. P.

The Eijkman Fermentation Test as an Aid in the Detection of Faecal Organisms in Water. L. W. Leiter. (*Amer. J. Hygiene*, 1929, 9, 705-724.)—Eijkman's test, consisting in the introduction of samples of water into dextrose-peptone broth and incubation at 46°, was carried out with a solution consisting of dextrose, 10; peptone, 10; sodium chloride, 5; and water, 75 per cent. The medium is sterilised at 10 lbs. pressure for 10 minutes at 110° C., and 1 part of medium is diluted with 7 parts of the water. For small quantities (10 c.c.) ordinary fish-hook fermentation tubes are used, and for large quantities a 250 c.c. flask fitted through the stopper with two U tubes, one reaching to the bottom of the flask and the other just through the stopper. The outer ends are drawn out and sealed. After sterilisation the sealed top of the shorter tube is broken, the flask filled with medium and sample, and the stopper replaced with pressure enough to expel all air. The tube is re-sealed, and the sealed end of the longer one broken. The whole is placed in the incubator with the end of the open tube over a beaker, to receive fluid expelled by formation of gas in the top of the flask. In testing the power of growth of pure cultures in the medium the concentration corresponding to above is given by using dextrose, 12.5; peptone, 12.5; sodium chloride, 6.25 grms.; and water, 1000 c.c. Eijkman's test was found to be selective for *Bacillus coli* and to inhibit or destroy other organisms ordinarily present in water. Strains obtained in pure culture from warm-blooded animal faeces produce typical gas, acid and growth reaction in the medium as a fairly constant characteristic,

but at 46° C. certain organisms, apparently *Bacillus coli*, isolated from cold-blooded animals do not produce a typical reaction under the same conditions. The fermentation in Eijkman's medium is correlated with the production of indol, the non-utilisation of sodium citrate and of the nitrogen in uric acid by strains of *Bacillus coli* isolated from warm-blooded animal faeces. The test is usually complete in 16–24 hours, and in 92·75 per cent. of positive Eijkman fermentation tests the presence of *Bacillus coli* can be confirmed, and positive tests yield members of the aerogenes-cloacae group infrequently, in marked contrast to the frequency of isolation by standard methods. Waters freely inhabited by cold-blooded animals, but not contaminated by warm-blooded animal faeces, may be passed by the Eijkman test and condemned by standard methods.

D. G. H.

Agricultural.

Application of the Strychno-molybdic Method to the Determination of Phosphoric Acid in Soil. C. Antoniani and S. Bonetti. (*Giorn. Chim. Ind. Appl.*, 1929, 11, 154–155.)—To determine the total phosphoric acid in soil by the strychno-molybdic method (ANALYST, 1928, 53, 405, 605), 20 grms. of the soil are heated to boiling for an hour in a 500 c.c. measuring flask with 30 c.c. of hydrochloric acid (1·18), 20 c.c. of nitric acid (1·40) and 50 c.c. of water. The liquid is then cooled, made up to volume with water, mixed, and filtered through a pleated filter. Of the filtrate, 50 c.c. are made neutral to phenolphthalein by addition of 10 per cent. sodium hydroxide solution, the slight precipitate of basic salts being redissolved by adding a few drops of 10 per cent. nitric acid. The resulting clear solution is mixed with 45 c.c. of the strychno-molybdic reagent and, after standing for about an hour, the precipitate is collected on a dried and weighed Gooch crucible, washed with 100 c.c. of dilute nitric acid (10 c.c. of 1·40 acid made up to 100 c.c.), and dried to constant weight in a water-oven. Multiplication of the weight of the precipitate by 0·0257 gives the weight of P_2O_5 , and further multiplication by 0·983 corrects for the volume occupied by the soil in the 500 c.c. flask.

To determine the P_2O_5 soluble in 1 per cent. citric acid solution, 100 grms. of the soil are shaken for 5 hours in a 1000 c.c. flask with 750 c.c. of the citric acid solution and left for 12 hours to settle. The liquid is filtered, if necessary, and 250 c.c. are evaporated to dryness, the residue being gently calcined with a few crystals of ammonium nitrate until all organic matter is oxidised. The residue is then dissolved in a little water containing a few drops of nitric acid, and the liquid heated on a water-bath for some minutes and filtered. The neutralised filtrate is then treated as described above.

T. H. P.

Organic Analysis.

Menthone as a Reagent for Aldehydes. D. Vörländer. (*Z. anal. Chem.*, 1929, 77, 241–268.)—Menthone is prepared by heating a solution of 23 grms. of sodium in 400 c.c. of absolute alcohol with 170 grms. of malonic acid ester and

100 grms. of freshly distilled mesityl oxide (b.pt. 126 to 131° C.) for 2 hours under a reflux condenser, and for a further 6 hours after the addition of 700 grms. of 18 per cent. potassium hydroxide solution. After neutralisation of the solution to litmus with dilute hydrochloric acid the alcohol is distilled off, the solution decolorised with charcoal, and the menthone (130 grms.) is precipitated from the pale-yellow, neutral solution by boiling it for 1 minute with sufficient dilute hydrochloric acid to render the reaction acid to methyl orange. It is filtered off and washed in the cold, treated with charcoal and recrystallised from acetone-water as pale yellow monoclinic crystals, soluble in petroleum spirit. When heated it reddens if freshly prepared, and decomposes at the m.pt. (148 to 150° C.). A saturated aqueous solution contains 0.4 gm. per 100 c.c. at 20° C. and deposits white crystals, m.pt. 200° C. (with decomposition), on standing, and is eventually converted into dimethyl glutaric acid. Warm saturated solutions of menthone, but not its esters or anhydride, give characteristic crystalline precipitates of the type (aldehyde + 2 menthone-H₂O) with aldehydes. These are enolic di- or triphenyl methanes which, on treatment with alcohol, glacial acetic acid or concentrated sulphuric acid, lose another molecule of water and form characteristic, non-acidic anhydrides (xanthone compounds) which do not give a brown colour with ferric chloride solution. Methods of preparation and properties of numerous aldehyde-menthones and their anhydrides and derivatives are fully described. The following are included, figures in brackets representing the corr. m.pt.s. of the menthone compound and its anhydride, respectively:—*Formaldehyde* (189° C., 171° C.). 0.00005 per cent. solutions yield a haze after 6 hours in contact with warm, saturated solutions of menthone. *Acetaldehyde* (139° C., 174° C.) reacts at room temperature, and the method may be used for the detection and determination of it in wood distillation products. *Propionic aldehyde* (155° C., 143° C.) is also precipitated quantitatively. *Isovaleraldehyde* (80 to 90° C., 172° C.). *Oenanthaldehyde* (103° C., 112° C.). *Acrolein* (186 to 192° C., 163° C.). *Crotonaldehyde* (183° C., 166° C.). *Citronellal* (78° C., 173° C.). *Citral* gives a very indefinite reaction. *Glycolaldehyde* (237.5° C.) gives the same condensation product with menthone (C₁₈H₂₄O₄) as is obtained by reaction with *monochloroacetaldehyde*, one molecule each of water and hydrochloric acid being removed in the latter case. It forms a characteristic acetyl derivative, m.pt. 206° C. *Glycer-aldehyde* (197.5° C., 172° C.). A 0.001 per cent. solution is detectable. *Glyoxaldehyde* (186° C., 224° C.). *Methylglyoxaldehyde* (164° C.). *Lactic aldehyde* gave no reaction. *Malonaldehyde* (237° C.). *Benzaldehyde* (see *Ann. der Chem.*, 1899, 309, 379). *Cinnamaldehyde* gives (1) white prisms, m.pt. 213° C. (turning yellow) in hot alcoholic solutions, and (2) fine crystalline yellow plates, m.pt. 161° C., with the same formula (C₂₅H₂₈O₃) in cold solution. Acetic anhydride converts both into the same anhydride, m.pt. 175° C. *Coumaraldehyde* (171° C., 173° C.). *p-Hydroxybenzaldehyde* (190° C., 246° C.). *p-Anisaldehyde* (145° C., 243° C.). *Salicylaldehyde* (208° C., 191° C.). *o-Chlorbenzaldehyde* (205° C., 225° C.). *Vanillaldehyde* (197° C., 228° C.). *Piperonaldehyde* (178° C., 220° C.). *Furfuraldehyde* (160° C., 164° C.). *Isatin* (284° C.).

J. G.

Determination of Ethylene by Absorption in a Solution of Silver Nitrate. V. N. Morris. (*J. Amer. Chem. Soc.*, 1929, **51**, 1460-1462.)—By means of the author's absorption apparatus (*id.*, 1927, **49**, 979) 12 c.c. of a 40 per cent. solution of silver nitrate will remove 35 c.c. of ethylene from 50 c.c. of a mixture of ethylene and nitrogen in 1 minute. Larger quantities of more dilute solutions (up to 80 c.c. of a 5 per cent. solution) give slower absorptions, but in all cases the results agree with those obtained with other absorbents less convenient to handle. The ethylene may be recovered by evacuation, and if acetylene is present it may be determined by titration of the nitric acid liberated. J. G.

Identification of Ortho-, Meta- and Para-Hydroxybenzoic Acids. F. F. Blicke and F. D. Smith. (*J. Amer. Chem. Soc.*, 1929, **51**, 1947-1949.)—During the course of some recent work in which it was necessary to isolate, purify and identify small amounts of *o*-, *m*- and *p*-hydroxybenzoic acids, unsatisfactory results were obtained by the use of the method of Lyman and Reid (*J. Amer. Chem. Soc.*, 1917, **39**, 704) for the identification of these acids. In this method the acids are converted into their sodium salts, and these, dissolved in a mixture of water and alcohol, are heated with *p*-nitrobenzyl bromide to give the *p*-nitrobenzyl esters. The authors have found that the esters, as soon as they are formed, react to some extent with *p*-nitrobenzyl bromide to form the *p*-nitrobenzyl ethers, that is, the dinitrobenzyl derivatives of the hydroxy acids. The substance described by Lyman and Reid as the *p*-nitrobenzyl ester of *p*-hydroxybenzoic acid, is now shown to be the dinitrobenzyl compound. The esters, or mononitrobenzyl compounds, are very soluble in organic solvents, but the dinitrobenzyl derivatives are much less soluble, and can be recrystallised readily from acetone. The method has therefore been modified in such a way that the formation of the dinitrobenzyl products is favoured. Compounds have been formed which can be recrystallised with less loss of material, and since the dinitrobenzyl derivative has a higher molecular weight than the mononitrobenzyl compound, a larger amount of material, in the case of the former substance, can be obtained from a given weight of the hydroxy acid. Furthermore, by the use of the dinitrobenzyl derivatives, it is possible to separate a mixture of two isomeric hydroxybenzoic acids; the derivative of the *p*-hydroxy acid is quite insoluble in acetone, that of the meta acid more soluble, whilst the ortho isomer is fairly soluble. Details are given of the preparations, melting points and analyses of the di-*p*-nitrobenzyl derivatives, the *p*-nitrobenzyl esters and the *p*-nitrobenzyl ethers of hydroxybenzoic acids.

P. H. P.

Studies on the Combination between certain Basic Dyes and Proteins. L. M. C. Rawlins and C. L. A. Schmidt. (*J. Biol. Chem.*, 1929, **82**, 709-716.)—In a previous communication by Chapman, Greenberg and Schmidt (*J. Biol. Chem.*, 1927, **72**, 707) studies were reported on the nature of the combination which takes place between certain acid dyes and proteins. Gortner (*J. Biol. Chem.*, 1927, **74**, 409) took exception to the interpretation given to the data presented, and considered that they confirmed his own conclusions. A reply to his criticism

would necessitate the opening of the question as to the exact definition of adsorption, so the authors prefer to let the matter rest, and believe that they and others have found sufficient evidence to place the reaction between proteins and acids or bases (*i.e.* acid or basic dyes) in the category of true chemical reactions. The present investigation is a continuation of that previously reported by Chapman, Greenberg and Schmidt. Casein, fibrin and gelatin were each titrated with methylene blue, safranin Y, and induline scarlet. Edestin was titrated with methylene blue and safranin Y, but not with induline scarlet, as its manufacture was discontinued after the work was begun. Titration curves show that in the region of $P_{H}11$, gelatin binds 70×10^{-5} equivalents of dye, casein 210×10^{-5} , edestin 70×10^{-5} , and fibrin 168×10^{-5} equivalents. Within limits of error and taking into account the possibility of modification of the protein taking place at high alkalinities, a correlation between certain groups in the proteins studied and their capacity for binding base can be made. This correlation suggests that the union between protein and basic dye, under the experimental conditions observed, takes place in stoichiometric proportions.

P. H. P.

Determination of Insoluble Matter in Tanning Extracts. C. Riess. (*J. Inter. Soc. Leather Trades Chem.*, 1929, 13, 246.)—The disadvantages involved in the ordinary methods for determining the insoluble matter in extracts, namely, the trouble of thoroughly cleaning the filter candle, and the time required for and uncertainty of obtaining clear filtrates with filter paper, would appear to be largely overcome by the adoption of the following apparatus:—A Büchner funnel is fitted with an adapter which is attached to a piece of thick-walled glass tubing, 120 cm. long and 2 mm. internal diameter. A suspension of 1 gm. of kaolin clay in 75 c.c. of the tannin solution is poured on to the filter paper in small portions at intervals. The funnel is then filled with fresh solution. As soon as the filtrate becomes optically clear (25 to 50 c.c.) the requisite amount is rejected, and 50 c.c. of the next 60 c.c. are taken for the evaporation. The 120 cm. column of solution causes a partial vacuum to form, thus accelerating filtration, and the apparatus is easily prepared for subsequent analyses.

R. F. I.

Inorganic Analysis.

Detection and Determination of Carbon Disulphide in Air. E. Selivounoff. (*Ann. Chim. anal.*, 1929, 11, 133.)—Carbon disulphide may be determined in the atmosphere by aspirating air at the rate of 10 litres an hour through two flasks containing 10 per cent. potassium or sodium hydroxide solution, then through 2–5 per cent. sulphuric acid, and lastly through two wash-bottles containing 5 per cent. alcoholic potassium hydroxide solution. Hydrogen sulphide, sulphur dioxide, carbon dioxide and hydrocyanic acid are thus eliminated. The carbon disulphide is held by the alcoholic potash, and potassium xanthate is produced. This solution is reduced to half its volume at 80°C ., neutralised with 5–10 per cent. acetic acid, with 1 drop of phenolphthalein, 0.5 to 1 c.c. of an alcoholic solution of guaiacum resin added, and the liquid titrated, drop by drop,

with 0.0002 *N* copper sulphate solution in a test tube without shaking. When the blue colour spreads through the whole liquid the titration is finished. One c.c. of the copper solution equals 0.011 mgrm. of carbon disulphide; the method is suitable for 0.001 to 0.002 mgrm. of carbon disulphide. D. G. H.

Reaction for Primary Arsines. S. S. Nametkin and W. Nekrassow. (*Z. anal. Chem.*, 1929, 77, 285–289.)—If 3 drops of clear saturated hydrogen sulphide water are added to 1 c.c. of an aqueous solution of a primary arsine a white opalescence is produced (easily visible against a white ground), which may be extracted with ether. The reaction, which has been used to detect 0.05 mgrm. of methyl-, ethyl-, β -chlorvinyl-, and phenyl-dichlorarsines, follows the equation (Baeyer, 1858) $\text{RAsCl}_2 + \text{H}_2\text{S} = 2\text{HCl} + \text{RAsS}$. The reagent, which in alcoholic solution is less sensitive and produces crystalline deposits, will remain clear for a month if it is filtered after addition of 1 drop of sulphuric acid. Ferrous, copper, cadmium, nickel and zinc sulphates, potassium chromate, lead cobalt and bismuth nitrates, and ferric, stannous and mercuric chlorides do not influence the test appreciably, but mercurous nitrate solution gives white, grey or black precipitates of calomel or reduced mercury, or both, with aqueous solutions of these arsines. This reagent, though less sensitive, may be adapted to distinguish different arsines. J. G.

Use of Cresol Red in Acid Solutions. F. R. McCrumb and W. R. Kenny. (*J. Amer. Chem. Soc.*, 1929, 51, 1458–1459.)—Cresol red has an acid range from pH 0.2 to 1.8 (red to yellow) with a half transformation point at pH 1.0. Its solutions are more stable than those of methyl violet and are useful to test for free mineral acids or acidic salts in the presence of weak acids, and in qualitative analysis for the separation of the sulphides of the third and fourth groups. J. G.

Determination of Sulphur in Galena and Lead. H. Leysaht. (*Z. anal. Chem.*, 1929, 77, 209–213.)—This evolution method is based on solution of the material in hydrobromic acid (sp. gr. 1.49) containing a little stannous chloride to bind any free bromine. The liberated hydrogen sulphide is conducted into a receiver containing a cadmium solution (25 grms. of cadmium acetate and 200 c.c. of glacial acetic acid per litre). The cadmium sulphide precipitate is decomposed by 0.1 *N* iodine solution, the excess of free iodine being measured with thiosulphate. W. R. S.

Sensitive Test for Magnesium. W. L. Ruigh. (*J. Amer. Chem. Soc.*, 1929, 51, 1456–1457.)—Suitsu and Okuma's *o,p*-dihydroxy-azo-*p*-nitrobenzene reagent (*J. Soc. Chem. Ind. Japan*, 1926, 29, 132) is prepared by coupling diazotised *p*-nitraniline with a solution in dilute sodium hydroxide solution of the theoretical quantity of resorcinol. The dye is precipitated by acid, filtered off, and recrystallised from methyl alcohol (m.pt. 199 to 200° C.). The solution to be tested, containing at least 0.002 mgrm. of magnesium, is made just acid with hydrochloric acid, and one drop of a 0.5 per cent. solution of dye in 1 per cent. sodium hydroxide solution added; a sky-blue precipitate settles out when the mixture is made

alkaline or shaken. Excess of ammonium salts, which destroy the sensitiveness of the test, and nickel and cobalt (which give similar lakes) should be removed.

J. G.

Ceric Sulphate in Volumetric Analysis. VI. Oxidation of Hydrogen Peroxide by Ceric Sulphate. Indirect Determination of Lead. N. H. Furman and J. H. Wallace. (*J. Amer. Chem. Soc.*, 1929, 51, 1449-1453.)—Furman's potentiometric method (*cf.* ANALYST, 1929, 371) has been applied to the titration of ceric sulphate with hydrogen peroxide according to the equation $2\text{Ce}(\text{SO}_4)_2 + \text{H}_2\text{O}_2 = \text{Ce}_2(\text{SO}_4)_3 + \text{H}_2\text{SO}_4 + \text{O}_2$. Results with a mean error of ± 0.02 c.c. were obtained in the presence of 1.5 *N* nitric acid, or, for the reverse titration, of 1.0 to 3.0 *N* hydrochloric, sulphuric or acetic acid. The rise in voltage at the end-point is sharper for hydrochloric or acetic acid, but the visual end-point, which is usually 0.05 c.c. higher than that obtained potentiometrically, is obscured in the former case by the presence of iron. Lead peroxide may be determined by titrating the excess of hydrogen peroxide in a solution of 0.2 gm. of sample in 25 c.c. of standardised 0.1 *N* hydrogen peroxide and 25 c.c. of nitric acid (sp. gr. 1.42) free from oxides of nitrogen.

J. G.

Rapid Test for Tungsten in Ores. A. Petrovsky. (*Z. anal. Chem.*, 1929, 77, 268-269.)—A powdered ore containing 0.5 per cent. or more of tungsten yields a blue colour when 0.2 gm. is reduced by the action of a piece of lead and 2 c.c. of hot concentrated hydrochloric acid for 2 minutes. On the addition of 15 c.c. of water a blue precipitate of the pentoxide forms, which may appear green or brown with small amounts of tungsten. Similar reduction of niobium gives a similar but duller colour, which disappears on dilution; titanium gives a green colour which disappears on standing or turns pale violet, whilst vanadium is distinguished by the fact that reduction to a blue compound may be effected by tartaric acid. Molybdenum gives no reaction.

J. G.

Separation of Tungsten from Vanadium. A. Jilek and J. Lukas. (*Czechoslovak Chem. Communications*, 1929, 1, 263-274.)—The method is based on the precipitation of quinine arsenotungstate in presence of vanadyl salt. The neutral solution (100 c.c.), containing less than 0.2 gm. of WO_3 and 0.1 gm. V_2O_5 , is acidified with 1 c.c. of hydrochloric acid and boiled with 0.5 gm. of hydroxylamine hydrochloride for the reduction of the vanadate; it is then treated with 10 c.c. of 2 per cent. arsenic acid and another c.c. of hydrochloric acid, diluted to 200 c.c., boiled, stirred, and precipitated with 20 c.c. of 2 per cent. quinine hydrochloride solution. Next day, the precipitate is collected and washed with water containing a little arsenic and hydrochloric acids and quinine hydrochloride, and finally with acidulated water containing a little of the precipitant, and ignited in platinum. The oxide is evaporated with nitric acid and ignited to constant weight. With large amounts re-precipitation is advisable. For the determination of the vanadium, the organic matter in the filtrate is destroyed with sulphuric acid and copper oxide; copper and arsenic are precipitated as sulphides; the filtrate is made alkaline and oxidised with hydrogen peroxide, neutralised, and precipitated with mercurous nitrate.

W. R. S.

Zirconium. IV. Precipitation of Zirconium by Phosphates. R. D. Reed and J. R. Withrow. (*J. Amer. Chem. Soc.*, 1929, 51, 1311–1315.)—Phosphoric acid, ammonium phosphate or microcosmic salt in five-fold excess are equally efficient for the quantitative precipitation of zirconium as phosphate, and more efficient than sodium phosphate, a forty-fold excess of which will, however, remove practically all the zirconium after a long period of standing and does not interfere with subsequent tests for potassium. The best results were obtained in the presence of 0.35 to 0.65 *N* sulphuric acid, 0.27 *N* nitric acid or 0.2 *N* hydrochloric acid being less suitable, whilst removal was incomplete in the absence of acid. The procedure was to allow the precipitated solution to stand over-night, and then to filter on a fine paper, and to test the warm, concentrated filtrates and washings for zirconium by neutralisation with ammonia (*cf.* ANALYST, 1929, 370). J. G.

Volumetric Determination of Vanadium by Means of Potassium Iodate. E. H. Swift and R. W. Hoeppel. (*J. Amer. Chem. Soc.*, 1929, 51, 1366–1371.)—The vanadate solution (25 c.c.) is well shaken in a flask, and carbon dioxide blown rapidly over the liquid to remove oxygen. It is then rendered 6 to 8 *N* with respect to hydrochloric acid by addition of oxygen-free 12 *N* acid. Carbon tetrachloride (5 c.c.) and a measured excess of standardised iodate-free potassium iodide solution are added, the flask stoppered, and the mixture titrated rapidly after a few minutes with a standard 0.025 *M* solution of potassium iodate until no more colour is visible in the solvent. Acid is added during titration to keep the concentration above 6 *N*. Under these conditions quadrivalent vanadium is not oxidised by the iodine monochloride formed by interaction of the hydrochloric acid, iodate, and iodine liberated according to the equation $\text{H}_3\text{VO}_4 + \text{HI} + 2\text{HCl} = \text{VOCl}_2 + \frac{1}{2}\text{I}_2 + 3\text{H}_2\text{O}$. The method may be used in the presence of tungstic acid, phosphates, arsenates or ferric iron, but tungstic acid must be held in solution by addition of phosphoric acid. J. G.

Chlorate Method for determining Nitrate Nitrogen, Total Nitrogen, and other Elements in Soils and Plant Tissues. E. M. Emmert. (*J. Assoc. Off. Agric. Chem.*, 1929, 12, 240–247.)—The chlorate method allows of the rapid and accurate determination of nitrate and total nitrogen in plant tissues and soils, and gives a residue in which other inorganic elements may be determined. Sufficient of the dry sample—ground to pass a 50-mesh sieve and leave the green tissue intact—to yield 0.5–1 mgrm. of nitrate nitrogen is placed in a 500 c.c. Kjeldahl flask and washed down with 25 c.c. of 50 per cent. (vol.) sulphuric acid. The flask is joined to a condenser, the free end of which leads through a two-holed rubber stopper into an absorption tower containing 150 c.c. of freshly prepared, yellowish-green chlorine dioxide solution, made by dropping concentrated hydrochloric acid on to sodium chlorate and passing the gas into water. The exit from the tower is fitted with a trap into which part of the liquid is forced during the action. The flask is heated to expel the gases rapidly but not violently into

the tower. Distillation is carried out quickly as soon as water vapour condenses, foaming ceases, and little gas is evolved, and the distillation is continued until white fumes appear. The flask is disconnected before the flame is extinguished, and the residue is saved for the determination of reduced nitrogen.

The condenser, trap and tubes are washed out with water, and fresh chlorine dioxide solution is added, if necessary, to make the solution in the tower yellow. The solution is at once boiled until colourless and made up to a definite volume. An aliquot part containing at least 0.25 mgrm. of nitrate nitrogen is treated, while hot, with 0.05–0.1 grm. of silver sulphate, and shaken now and then during five minutes, 0.5–1 grm. of lime being then added. After being again shaken occasionally for a few minutes, the liquid is filtered bright and an aliquot part containing at least 0.2 mgrm. of nitrate nitrogen evaporated to dryness. The residue is covered with 2–3 c.c. of phenoldisulphonic acid, left for 5–10 mins., and treated with 20–30 c.c. of water until most of the salts dissolve. A few c.c. more 25 per cent. sodium hydroxide are added than is necessary to give a yellow colour, the liquid being made up to 100 c.c., shaken with 0.5 grm. of calcium hydroxide, and filtered. A standard containing 0.0025 mgrm. of nitrogen per c.c. is used for comparison, the volume of the unknown being suitably adjusted. The method gives consistent results and determines added nitrate nitrogen accurately, but much lower results were obtained with certain soils than were found by the official method.

To determine reduced nitrogen, either the cold residue in the Kjeldahl flask, together with 10 c.c. of water, or a smaller amount of fresh sample is boiled for about 5 mins. with 20 c.c. of 50 per cent. (vol.) sulphuric acid until it is charred and all nitrate nitrogen is expelled. The cooled mass is treated with 10 c.c. of water, again cooled, shaken with 1 grm. of sodium chlorate for each 0.1 grm. of dry tissue or 0.5 grm. of green tissue or soil, and heated rapidly until the green chlorine peroxide fumes are decomposed and only white fumes remain; if the green fumes are excessive, special care is taken, as explosion may occur at about 100° C. The liquid is placed in the apparatus described above and, when violent action ceases, is distilled into water in the absorption tower. The Kjeldahl flask is disconnected when the solution remains colourless and white fumes form. The procedure is then as described for nitrate nitrogen.

To determine total nitrogen, a still smaller sample is placed in a Kjeldahl flask, with sodium chlorate at the same rate as for reduced nitrogen, and 25 c.c. of the 50 per cent. sulphuric acid. The heating and distillation are effected similarly, collection of masses of chlorate over the flame being prevented. The nitrate nitrogen is determined as described above.

The residue in the flask, when freed from sulphuric acid by distillation, serves for the determination of any non-volatile element except sodium and sulphur; sodium may be determined if potassium instead of sodium chlorate is used. The carbon appears to be evolved as carbon dioxide during the distillation, and preliminary experiments indicate that it may be determined by absorbing the gas in soda-lime.

T. H. P.

A more Stable Alcoholic Potash Reagent for Saponification. D. T. Englis and V. C. Mills. (*J. Assoc. Off. Agric. Chem.*, 1929, 12, 248-251.)—To 2 litres of alcoholic potash reagent, prepared according to the official method, 10 grms. of sodium hydrosulphite were added, the solution being mixed and left undisturbed, except for an occasional shaking, for about a year in a stoppered flask. Determinations of the saponification values of several oils, then made with the clear, almost colourless supernatant liquid, gave results in close agreement with those obtained by the official reagent. It has not been found possible to discover a general inhibitor of the development of colour during the saponification process.

T. H. P.

Volumetric Determinations by Iodate. A. Schwicker. (*Z. anal. Chem.*, 1929, 77, 161-169.)—Sulphurous acid reacts with acidified iodate solution in two stages: (1) $2\text{HIO}_3 + 5\text{H}_2\text{SO}_3 = 5\text{H}_2\text{SO}_4 + \text{H}_2\text{O} + \text{I}_2$; and (2) $\text{H}_2\text{SO}_3 + \text{I}_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + 2\text{HI}$. The sulphite solution is run from a burette into a measured excess of 0.1 *N* iodate solution acidified with hydrochloric or sulphuric acid. The liquid is then treated with excess of potassium iodide and the liberated iodine titrated with thiosulphate as usual. Hydrazine, ferrocyanide, thiocyanate, arsenious and antimonious oxides, can be determined volumetrically by means of the same technique, for details of which reference is invited to the original paper.

W. R. S.

Iodimetric Determination of Thiocyanates. A. Schwicker. (*Z. anal. Chem.*, 1929, 77, 278-280.)—A measured quantity of a solution of the sample is made alkaline with 5 to 10 c.c. of *N* ammonium borate solution (170 grms. of 10 per cent. ammonia and 20 grms. of boric acid per litre) and allowed to react with a measured excess of 0.1 *N* iodine solution for 2 minutes. It is then acidified with 10 c.c. of 2 *N* acid, and the residual iodine titrated with 0.1 *N* sodium thiosulphate solution in the presence of starch. The borate solution increases the velocity of the reaction— $\text{CNS}' + 3\text{I}_2 + 4\text{H}_2\text{O} \rightarrow \text{SO}'_4 + 6\text{I}' + 8\text{H}' + \text{CN}'$, and is preferable to ammonia or ammonium chloride for this purpose. An accuracy of 0.02 c.c. of iodine solution is obtainable.

J. G.

Physical Methods, Apparatus, etc.

Zinc Sulphide Method of Measuring Ultra-violet Radiation, and the Results of a Year's Observations on Baltimore Sunshine. J. H. Clark. (*Amer. J. Hyg.*, 1929, 9, 646-662.)—The author's method for measuring the intensity of ultra-violet radiation by the rate of darkening of lithopone is modified, use being made of zinc sulphide, moistened with saturated lead acetate solution. Chemically pure zinc sulphide, when prepared by different methods, varies in its sensitiveness towards ultra-violet radiation. A standard grade, known as "ZnS ignited," has been developed by the J. T. Baker Chemical Company, and is highly satisfactory for this determination. A spatula-full of the zinc sulphide powder is moistened in a small mortar with a few drops of saturated lead acetate

solution and ground to a soft paste, which is placed on a piece of glass and pressed flat under a plate of transparent quartz. The glass and quartz are held together by elastic bands, and the paste is exposed normally to the radiation through the quartz. As the paste darkens somewhat on exposure to air, fresh material should be used for each observation.

Before exposure the paste has a reflexion factor of 76–78 per cent. It darkens rapidly and irreversibly on exposure to ultra-violet radiation. After exposure of 1, 2, 3, etc., minutes, the reflexion factor is determined with a Macbeth illuminometer, or, failing this, with a set of standard grey papers. The curve of darkening thus obtained gives the time required to produce darkening to a 50 per cent. reflexion factor, which is taken as that giving one ZnS unit of ultra-violet radiation; the intensity of the radiation is inversely proportional to the time required to give one unit. In practice, a set of typical darkening curves will indicate the time to give one unit from a single observation.

With sunlight and with mercury arc-light filtered through a Corning G 986 A filter, one ZnS unit equals one lithopone unit, but with the bare mercury arc one ZnS unit equals 1.33 lithopone unit. For zinc sulphide the temperature coefficient of darkening,

$$Q_{10} = \frac{\text{velocity at } (T+10) ^\circ\text{C.}}{\text{velocity at } T ^\circ\text{C.}}, \text{ has the value about } 1.2,$$

If this method is used to measure the intensity of a quartz mercury arc, wave-lengths not greater than $313\mu\mu$ are alone effective. With solar radiation the method is less satisfactory, as the darkening is then due to a band $290\text{--}350\mu\mu$, with the maximum effect at $320\mu\mu$. Marked therapeutic effect is produced only by waves of $290\text{--}310\mu\mu$, and only about one-sixth of the energy measured lies in this region, although the value of this fraction varies greatly throughout the year.

Measurements of solar ultra-violet radiation made in Baltimore during 15 months by the zinc sulphide method gave results comparing favourably with those of other methods and show that there is maximum intensity in August and minimum in January, the ratio between the two being 8:1.

T. H. P.

New Method of Mounting Vegetable Powders for Microscopical Examination. W. O. Howarth. (*Pharm. J.*, 1929, 122, 522–523.)—A little of the powder (stained according to the type of material) is mixed with a drop of a mounting medium composed of: carbolic acid, 20; lactic acid, 20; glycerin, 40; and water, 20 parts. The slide is covered and allowed to stand for a few minutes, or it may be warmed. All details of cell structure are brought out perfectly. For permanent preparations as much as possible of the liquid is drained off, glycerin jelly added, and the cover slip ringed round with gold size. Sections may also be mounted in the same medium. For staining powders containing leaves, fruits, seeds and soft tissues generally, aniline blue may be used; for lignified tissues, cotton red stain (a form of safranin).

References to Scientific Articles not Abstracted.

COMPOSITION OF WATER AND MOSQUITO BREEDING. By W. RUDOLFS and J. B. LACKEY. *Amer. J. Hyg.*, 1929, 9, 179.

Attempts to correlate chemical composition of water, and biological growth therein, with the breeding of larvae of *C. pipiens*—Gradual change of the reaction of water did not affect growth—Breeding absent when protozoa, fungi, etc., were low in amount—Breeding not affected by ratios of carbon to nitrogen in the water—Specific substances formed by decomposition of vegetable matter may be a promoting cause.

THE PROPERTIES AND APPLICATIONS OF "VITA" GLASS. By F. E. LAMPLOUGH. *J. Roy. Soc. Arts*, 1929, 77, 799 (June 28th).

"Vita" glass transmits rays between 3000 and 3200 Å.U.—Tests of permeability—Use of fluorescent substances in testing—Therapeutic effects—Initial deterioration—Stability reached in about a month—Approximate efficiency figure (for 2 mm. thickness) is then about 65 per cent. at 3130 Å.U.—Loss due to reflection at the two glass surfaces (about 8 per cent.) and to absorption—Glass for window purposes must be resistant to atmospheric influences.

THE ACTION OF THALLIUM. *Brit. Med. J.*, 1929, 962 (May 25, 1929).

A summary of the literature on the physiological action of thallium—Use as a depilatory has become popular—Fuld (*Muench. med. Woch.*, 1928, 75, 1124) describes mild and fatal cases of poisoning—Dixon (*Proc. Roy. Soc. Med.*, 1927, 20, 1197) demonstrated that the action is not locally upon the hair follicles but upon the cells—Case of acute poisoning by thallium rat paste described by Greving and Gagel (*Klin. Woch.*, 1928, 7, 1323)—Histological effects described by Buschke (*Klin. Woch.*, 1928, 7, 1515)—Effects of chronic industrial poisoning studied by Buschke (*Med. Klin.*, 1928, 24, 1042), and by Teleky (*Wien. med. Woch.*, 1928, 78, 505)—Lutz (*Zeit. Gewerbehyg. u. Unfallverhütung*, 1928, 15, 172) found that thallium acetate (5 per cent.) ointment, when applied to rabbits and guinea-pigs, caused death in 4 days—Cumulative action with small doses—Use of gloves advisable when handling thallium salts.

Reviews.

BAYLEY'S CHEMISTS' POCKET BOOK. Edited by ROBERT ENSOLL. Ninth Edition. Pp. xvi+460. Price 8s. 6d. net.

The ninth edition of this useful book of reference has been revised throughout. Certain sections, including those on mathematical conversions, chemical analysis and hydrogen ion concentration have been considerably amplified.

While the book is a mine of useful information, both chemical and general, it provides several examples of the folly of striving to include too much in a book of this character, with the attendant results of over-compression. When a compilation of this character attempts to invade the province of the text-book it necessarily fails. Thus, while it is obviously necessary that, when certain tables of analytical constants, such as those used in sugar analysis, are published, the methods of analysis should be plainly indicated, it is not clear what purpose is

served by the inclusion of some of the condensed descriptions of methods of analysis. The treatment of the whole subject of oil and fat analysis in a page and a half can hardly be adequate for the needs of any variety of chemist.

The section on hydrogen ion concentration is a further example. The table on pp. 350-351 includes a number of indicators, the colour changes of which are not given. It also includes several mixed indicators without any indication that they are anything but simple, or of what their special uses may be. The table on p. 353 is out of date and should be revised so as to be more in accordance with modern practice. A more extended table of acids and bases giving the P_H of the end-points of titrations and the most suitable indicators should replace this table with great advantage.

Unfortunately, it is noticeable throughout the book that there has been a certain carelessness in the proof reading. There is frequent mis-spelling of proper names, *e.g.* Keppler, Schlipp, Devardos, and Ilosvoy, besides numerous misprints. One hopes that the figures are more reliable. Judging by the small proportion that one can check in a short time, they appear to be so.

In spite of these deficiencies, the amount of information published at so reasonable a price is remarkable, ranging from the Greek alphabet and the sizes of photographic plates to the calculation of compound interest, in addition to a large amount of matter of more direct concern to chemists. Indeed, the book abounds in useful hints and unusual information, not to be found elsewhere.

NORMAN EVERS.

STANDARD METHODS OF TESTING PETROLEUM AND ITS PRODUCTS. Second edition. Pp. xiv+137. Published by the Institution of Petroleum Technologists. London: W. Speaight & Sons, Ltd. 1929. Price 7s. 6d. net.

In the testing of complex commercial products, such as crude petroleum and the products derived from it, many of the tests used for which purpose are purely empirical and need strict uniformity of conditions in order to obtain concordant results, standard methods are essential, not only to prevent disputes between buyer and seller, but also to enable the properties of the products as determined by the tests to be strictly comparable with the results obtained in practice by the use of the products. Provided the standard tests and methods are drawn up and agreed upon by technical experts, scientifically qualified and thoroughly representative of all the interests involved, and are revised and amended from time to time in accordance with the growth of knowledge and experience, they are no hindrance but a help to progress. Such a series of test methods is contained in the book under review.

The book contains methods for the determination of specific gravity, colour, sulphur in various forms, calorific value, viscosity, aromatic content, acidity, flash-point and fire-point, volatility, burning properties (illuminating oil), carbon

residue, cloud-point and setting-point, hard and soft asphalt, demulsifying properties, sludging value, dielectric strength, paraffin wax content, softening point, ductility and penetrability (asphaltic bitumen), &c., &c., as applied to Gasoline, White Spirit, Benzol Mixtures, Kerosine, Long-Time Burning Oil for signal lamps, Gas Oil, Mineral Lubricating Oils, Transformer and Switch Oils, Fuel Oils, Asphaltic Bitumen and Asphaltites, Commercial Paraffin Scale and Refined Paraffin Wax, and Crude Petroleum.

The "Standardisation Committee" appointed by the I.P.T., and its co-opted members, under whose auspices the methods have been formulated and are revised from time to time, is composed of technologists of the highest standing and attainments in the petroleum industry, and includes representatives of Government Departments, the National Physical Laboratory, the leading petroleum companies and individual specialists and consultants, and is divided into sub-committees, each having charge of one of the six classes into which the products dealt with are divided. Not only methods, but also apparatus, are standardised. Grave variations in what been have regarded as standard instruments, such as the Redwood viscometer, have been dealt with, the dimensions and tolerances of the essential parts are now laid down, and provision has been made for their calibration and certification by the National Physical Laboratory.

Weight has been given to the valuable work done by the American Society for Testing Materials and the American Bureau of Standards, and many of the American methods of testing have been adopted. The British Engineering Standards Association have also co-operated with the Committee, to prevent overlapping, and have agreed to adopt the standard methods of the I.P.T. for the purposes of their specifications, so far as petroleum products are concerned. Assistance has also been afforded to the Committee by the principal firms of instrument makers and by the British Lampblown Scientific Glassware Manufacturers' Association. Standard methods of sampling are also laid down. The tests are very conveniently arranged, a reference letter being given to each of the products dealt with and the same reference number to the same test as applied to each particular product. Thus, the method for determining the viscosity of Gasoline (G) has the Serial Designation G8, and of Lubricating Oil (LO) the serial designation L.O.8. The book is interleaved throughout, for the purpose of making notes.

The volume, produced under the general editorship of Prof. J. S. S. Brame, assisted by Mr. Geo. Sell, the Secretary of the Committee, is of handy size, well bound and printed, and contains thirty dimensioned figures of apparatus described in the text. It is indispensable to every analyst whose practice includes the testing of the products with which it deals, and reflects credit on all concerned in its production.

L. ARCHBUTT.

VOLUMETRIC GLASSWARE. By VERNEY STOTT. Pp. 232. London: H. F. & G. Witherby. 1928. Price 20s.

The book under review deserves a place on the shelves of every laboratory in

which volumetric glass apparatus is used, especially where investigations requiring a high degree of volumetric accuracy are involved, for it contains much food for thought for the careful worker. It gives the history of the connection between the litre and the kilogramme and explains the reasons for the adoption of the units of volume, times of delivery and drainage of measuring vessels, and other standard conditions required by the National Physical Laboratory in the Tests for Volumetric Glassware. If there be any chemists who use glassware which has not been calibrated, as is alleged in the preface to the book, or who use pipettes or burettes capable of quick delivery, data are given in the book to show the risks they run when doing work of a high degree of accuracy.

After dealing with the distinctions between the millilitre and the cubic centimetre, and between the litre, the cubic decimetre and Mohr's litre, in a form familiar to those who have seen Report No. I on Units of Volume by the Joint Committee for the Standardisation of Scientific Glassware, the author works out the relationship between the volume in ml. and the weight in grms. in air, of water at different temperatures and barometric pressures.

Two tables are given by which an observer who possesses accurate gramme weights, knowing the weight of water in a litre vessel, and noting the temperatures of the water and air and barometric pressure, can find the correction to the nearest milligramme to be applied to the weight in order to find the numerical measure of the volume, in ml., at 15° C., of the vessel. These tables and similar tables in the last chapter, covering volumes ranging from 1 ml. to 2000 ml., enable one almost at a glance, and without elaborate calculations from the density of water, to calibrate quickly any vessel at temperatures ranging from 5.0° C. to 30.9° C., and barometric pressures from 730 to 790 mm. Another labour-saving table gives the factors, for the same temperature range, to connect weight of mercury with volume in ml. at 15° C.

Tables showing the actual amount of water, and of four common volumetric reagents, required to fill a graduated vessel at different temperatures give data for calculating the errors arising through use of standard liquids at temperatures different from that at which they were prepared. For instance, normal sulphuric acid prepared at 15° C. will be incorrect to the extent of 0.07 per cent. if used at 10° C., or of 0.2 per cent. if used at 23° C.

The methods used at the National Physical Laboratory for testing and marking flasks, burettes and other vessels are described and give useful information to users and manufacturers of these goods.

The data and curves showing the volume of water delivered and drained from pipettes and burettes in different times show the necessity for the slow-delivery tolerances adopted by the National Physical Laboratory. They should be carefully studied by every user of these vessels. Errors due to the use of quick-delivery milk-testing pipettes and of pipettes calibrated for water and used for solutions or for other liquids are shown in tables. Curves showing volumes delivered and drained from quick-delivery burettes show that appreciable errors may arise by

use at different rates of delivery, and, also that drainage for several minutes does not compensate for the differences in delivered volumes.

Consideration is given to the possible cumulative errors which may arise in various operations using National Physical Laboratory Class A vessels without corrections, but allowing the maximum tolerances in error.

Calibration of gas burettes by means of mercury, and for use with mercury is described, but no comment is made on meniscus errors due to different heights of mercury meniscus, nor on the calibration of closed gas-measuring tubes and the meniscus errors involved in their calibration and use.

Several typographical errors occur, two of which should be noted, namely:—"0-0000026" on page 27 should be "0-000026" and "one fifth" on page 123, line 5, should be "one fiftieth."

As a book of reference, its value is much reduced by the absence of an index, which may have been considered to be unnecessary in a book of this size, but would have been of great value in assisting a person who knows what is in the book to refer quickly to tables, tolerances allowed by the National Physical Laboratory, or other subject-matter. Then, again, the tables are as mysterious as they can be. Table I, page 24, gives a series of numbers corresponding with each tenth of a degree from 5-0° C. to 30-9° C., and Table II, on the following page, gives another series of numbers correlating degrees Centigrade with "pressures in millimetres of mercury at 0° C.," but there is no information on the table pages to indicate the significance of the temperatures or the units in which the corrections are expressed, and the reader has to search through several pages of letterpress for the information. If Table I had been headed "Table I, 1000 ml. correction in milligrammes to be added to observed weight in grammes, using brass weights, for various temperatures of water," it would have added greatly to the usefulness of the table. Similar headings on Table II, and on the thirty-two amplifications of these two tables at the end of the book would have been useful. Also, if one wants to find the connection between barometric pressure, as read, with that at 0° C., there is no hint until the last chapter is reached that there is a table on the last page of the book.

A. MORE.

ARTIFICIAL SILK. By Dr. O. FAUST. Translated from the German by E. FYLEMAN. Pp. v+184. Isaac Pitman & Sons. 1929. Price 10s. 6d. net.

A number of books dealing with artificial silk have appeared in the last few years. The majority of them were written by experts in the manufacture of artificial silk, so that the technical side was adequately treated. The authors, however, felt it necessary, in most cases, to include an account of the scientific basis of the industry. The treatment of this, in general, was far from satisfactory, and might, with advantage, have been omitted.

In the case of the little work now under review the author himself has obviously been trained on the scientific-research side of cellulose and artificial silk.

His book is based on the thesis that further progress in the manufacture of artificial fibres is dependent on an understanding and control of the basis—chemical, physical, colloidal—on which the industry is built. He therefore devotes about half the volume to the structure of cellulose and of artificial fibres as revealed by X-ray analysis and other methods, to the study of swelling power, the nature of the spinning process—particularly the stretch spinning process—and the ripening of viscose solutions.

The general section, Part I, covers 68 pages, and includes an account of the properties of cellulose, especially in relation to the size of the complex and its influence on the degree of solubility and viscosity of the cellulose and its derivative, the spinning solution, and the spinning process. In this chapter he refers briefly to his own investigations on the X-ray structure and double refraction of artificial silk threads. Another chapter deals with the lustre and colour of the threads, and a full chapter is devoted to swelling power and the determination of the degree of swelling of cellulose fibres in sodium hydroxide solutions in which he describes the methods of Weltzien and his own applications of them.

The technical section, Part II, deals briefly with raw materials, machinery, and spinning apparatus. Some account is given of Ost's experiments on the stretch spinning process, illustrated by a number of photographs showing the withdrawal of the thread at different speeds through nozzles of various dimensions. A few typical illustrations of German machinery are given. The chapters that follow deal with the individual methods of production, nitrate, acetate, viscose, and other silks. Each is considered under (a) theoretical, and (b) practical, the general chemistry and theory of the process being described first, followed by an account of the technical methods involved. The final chapter gives a brief survey of the economics of artificial silk, and a useful bibliography is included.

The feature of the book is its scientific treatment which, however, is useful not so much in regard to the definite facts it includes, as in the way it suggests to the reader problems for future research. The author's enthusiasm leads him, perhaps, to over-estimate the application of science. He refers particularly, for example, to the investigations of Karrer on the degradation of cellulose by the enzymes from the edible snail. These enzymes apparently enable silks from different German factories to be differentiated when all other tests fail. It is a little difficult to see the utility of such differentiation, except possibly in a criminal case. The book is quite well translated, though examples of involved sentences and German idiom are common. The following is an example—"this is less influenced by the distance traversed in the precipitating bath, although this also has some influence, because the concentration and temperature of the adhering precipitating bath which is carried along by the fibre, are constantly altering on account of the continued reaction." Some parts of the book also read like a collection of scraps taken from a note-book, *e.g.* the chapter on cellulose acetate, pp. 134-135.

The work is a useful contribution to the literature on artificial silk.

C. DORÉE.

QUESTIONED DOCUMENTS. By A. S. OSBORN. 2nd Edition. Pp. xxiv+1028. Albany, N.Y.: The Boyd Printing Co. London: Sweete & Maxwell. 1929. Price 55s. net.

Mr. Osborn's book, which has long been recognised as a standard work on the examination of documents, has, for some years, been out of print, and this new and enlarged edition should therefore meet with a wide welcome. The main features of the original edition have been retained. As before, the book opens with instructive chapters on the preliminary examination of documents and on standards of comparison. Then come chapters on photography and photographic methods, the microscope and its most suitable forms for examining documents, and on special measuring instruments, which include a "curve meter," a useful device of the author's for measuring and recording the shapes of curves.

The following chapters deal with handwriting and its variations, and the methods used in its examination, including the detection of traced and other forgeries. Paper and its water marks, the evidence of folds in paper, inks, pencil writing, and type-writing, are all discussed in detail, although, as the author makes no claim to chemical knowledge, his methods are mainly based on physical and optical measurements.

The way in which scientific evidence should be presented in Court is dealt with shrewdly and with humour, and stress is rightly laid upon the point that such evidence should be based on observed facts which can be demonstrated, and should not be allowed to degenerate into a "counting of heads," as it too often does when opinion is countered by opinion. These chapters will repay careful study by all who have to bring scientific reasoning before a judge or jury.

A new feature of this edition is a very full classified summary of legal citations of discussions on the facts and law relating to questioned documents, with references to the several judgments. Although this section of the book is mainly concerned with American law, yet much of what the author has so skilfully collated and indexed should be of use to lawyers and scientific witnesses in this country.

The bibliography, which was a valuable section of the first edition, has been retained and expanded, and, with its interesting accompanying commentaries now forms a fairly complete guide to the literature on handwriting and disputed documents. The subjects discussed in the 36 chapters are effectively illustrated with photographs and photographic enlargements, many of them relating to actual cases, and the book concludes with a good index.

This review gives only a slight indication of the immense amount of labour and thought which have contributed to the making of this book; and although we must differ from the author's conclusions on some of the technical questions, it is difficult to over-praise the work as a whole.

EDITOR.

Publications Received.

- THE ANALYSIS OF DRUGS AND CHEMICALS. By N. EVERS and G. D. ELSDON. London: Chas. Griffin & Co., Ltd. Price 25s. net.
- AN INTRODUCTION TO THE CHEMISTRY OF PLANT PRODUCTS. Vol. II. METABOLIC PROCESSES. By P. HAAS and T. G. HILL. 2nd Edition. London: Longmans, Green & Co. Price 10s. 6d. net.
- AN INTRODUCTION TO MODERN ORGANIC CHEMISTRY. By L. A. COLES. London: Longmans, Green & Co. Price 7s. 6d.
- THE PYROLYSIS OF CARBON COMPOUNDS. By C. D. HURD. New York: The Chemical Catalog Co., Inc. Price \$12.50.
- INDUSTRIAL CARBON. By C. L. MANTELL. London: Chapman & Hall. Price 21s. net.
- CRYSTAL STRUCTURE AND CHEMICAL CONSTITUTION. A General Discussion held by the Faraday Society. Price 8s. 6d.
- CHEMISTRY OF PULP AND PAPER MAKING. By E. SUTERMEISTER. New York: John Wiley; London: Chapman & Hall. Price 32s. 6d. net.
- ENZYME ACTIONS AND PROPERTIES. By E. WALDSCHMIDT-LEITZ. Translated and Extended by R. P. WALTON. New York: John Wiley; London: Chapman & Hall. Price 20s. net.
- INORGANIC QUANTITATIVE ANALYSIS. H. A. FALES. London: G. Bell & Sons. Price 12s. 6d. net.
- THE THEORY AND TECHNIQUE OF QUANTITATIVE ANALYSIS. By M. FARNSWORTH: New York: John Wiley & Sons; London: Chapman & Hall, Ltd. Price 12s. 6d. net.
- CHEMISTRY IN THE HOME. By J. B. FIRTH. London: Constable & Co. Price 5s. net.
- ANNUAL REPORTS OF THE SOCIETY OF CHEMICAL INDUSTRY ON THE PROGRESS OF APPLIED CHEMISTRY FOR 1928. Vol. XIII. Price, 12s. 6d. to non-members; 7s. 6d. to members.
- ANLEITUNG ZUR ORGANISCHEN QUALITATIVEN ANALYSE. By H. STAUDINGER. 2nd Edition. Berlin: Julius Springer. Price 6.60 Marks.
- PRACTICAL PLANT BIOCHEMISTRY. By M. W. ONSLOW. 3rd Edition. Cambridge: The University Press. Price 12s. 6d. net.
- DIZIONARIO DI MERCEOLOGIA E DI CHIMICA APPLICATA. 5th Edition. Vol. I. (ABELMOSCO-CUSCUTA). By G. VITTORIO VILLAVECCHIA. Milan: U. Hoepli. Price L.60.

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

The Determination of Organic Peroxides.

By S. MARKS, M.Sc., A.I.C., AND R. S. MORRELL, M.A., Ph.D., F.I.C.

(Read at the Meeting, May 1st, 1929.)

THE object of this investigation was to discover a reliable method for the determination of the peroxide-oxygen content of oxidised linseed oil and of certain oxidation products of the glyceride of β -elaeostearic acid (Morrell and Marks, *J. Oil and Colour Chem. Assoc.*, 1927, 10, 197). Fahrion employed the following method for the estimation of the peroxide-oxygen in oxidised linseed oil:

A sufficient quantity of the material is dissolved in glacial acetic acid, 1 c.c. of 50 per cent. sulphuric acid is added, and 2 c.c. of cold saturated potassium iodide solution. After standing for 1 hour the mixture is diluted with 50 c.c. of water, and the liberated iodine is titrated with $N/10$ sodium thiosulphate solution.

This method was first fully examined with the use of benzoyl peroxide as a criterion. A quantity of 0.2 to 0.3 grm. of the pure material, which had been crushed under dry ether and dried in a current of warm air, was dissolved in 25 c.c. of glacial acetic acid. (Glacial acetic acid is a good solvent both for partially oxidised linseed oil and other peroxides examined.) The reagents were added as set out in Table I, and the mixture allowed to stand in the dark. The product was diluted to about 100 c.c. with distilled water before being titrated, and a blank determination was made in each case.

The calculated peroxide-oxygen content of benzoyl-peroxide, $(C_6H_5COO)_2$, is 6.61 per cent.

TABLE I.

Estimation of peroxide-oxygen content of benzoyl peroxide in *glacial acetic acid* solution under various conditions.

Expt. No.	Amount of sulphuric acid (and water) added.	Amount of potassium iodide added.	Period of standing.	Temp.	Peroxide-oxygen found. Per Cent.
1	none	2 c.c. of saturated cold solution	10 minutes	Room	6.6
2	$\frac{1}{2}$ c.c. 98 per cent.	"	"	"	6.6
3	1 " "	"	"	"	6.4
4	2 " "	"	"	"	4.4
5	1 " 50 per cent.	"	"	"	6.7
6	1 " "	"	24 hours	"	6.6
7a	1 " "	"	48 "	"	7.3
7b	1 " "	"	" "	"	7.2
8	1 c.c. 50 per cent. + } 5 " water	"	10 minutes	"	7.1
9	1 c.c. 50 per cent. + } 7 " water	"	" "	5°-10° C.	6.2
10	1 c.c. 50 per cent. + } 11 " water	"	24 hours	5°-10° C.	4.1
11	none	2 grms. solid	48 "	"	7.3
12	"	"	1 "	50° C.	6.7

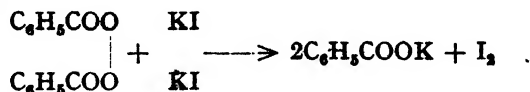
The following conclusions can be drawn from the above series of experiments:

(1) A theoretical result is obtained thus (Expt. No. 1): Dissolve 0.2 gm. of the peroxide in 25 c.c. of glacial acetic acid; add 2 c.c. of concentrated cold potassium iodide solution (or 2 grms. of the powdered solid); mix and allow the mixture to stand for a few minutes; dilute with about 100 c.c. of distilled water, and titrate with *N/10* sodium thiosulphate solution. A blank test must be made, and its result deducted. Ordinary potassium iodide (not necessarily free from iodate) and ordinary pure sulphuric acid were employed in the above experiments, but it is recommended to use both these reagents of "A.R." purity.

(2) The quantity of sulphuric acid added, if any, should not exceed 0.5 c.c., and either concentrated or 50 per cent. acid can be employed (compare Experiments 1 to 5). The potassium liberated from the potassium iodide forms potassium benzoate in the absence of sulphuric acid (see equation below); hence addition of sulphuric acid is unnecessary (Expt. 1), but in applying this method to other organic peroxides, linoxyn for example, which do not yield an acid to correspond to benzoic acid, the addition of sulphuric acid to the reaction mixture will be necessary.

(3) When the substance under examination dissolves readily in glacial acetic acid, no advantage is gained (a) by allowing the mixture to stand for 24 hours, (b) by heating the mixture above room temperatures, or (c) by cooling it.

EFFECT OF THE PRESENCE OF SULPHURIC ACID.—The low results obtained in the presence of increasing quantities of (a) concentrated sulphuric acid (Expts. 1–4) and (b) water (Expts. 9–10) are striking, and it is worthy of note in this connection that Baeyer and Villiger (*Ber.*, 1901, **24**, 740), using "angesäuerte Iodkaliumlösung" (no concentrations are mentioned) in the estimation of ethyl hydrogen peroxide, C_2H_5OOH , obtained only 21.07 per cent. of peroxide-oxygen, against a calculated value of 25.81 per cent. It might be supposed at first that excess of sulphuric acid produces low results by inhibiting the hydrolysis of the peroxide, but this supposition is untenable, because benzoyl peroxide liberates iodine directly in the absence of water, thus:



without previously undergoing hydrolysis to benzoyl peracid, C_6H_5COOOH . This is shown by (i) Expt. 11, (ii) Expts. 13, 15, 16 (below) carried out in acetic anhydride solution, and (iii) the fact that addition of dry benzoyl peroxide and dry potassium iodide to sodium-dried alcohol or ether is followed in each case by immediate evolution of iodine (see also Gelissen and Hermans, *Ber.*, 1926, **59**, B, 63).

EFFECT OF WATER.—In order to decide, if possible, the effect of water on the course of the reaction a series of experiments was next carried out with acetic anhydride as solvent in place of glacial acetic acid. The former has the advantage of dissolving benzoyl peroxide more readily. The peroxide (0.2 grm.) was dissolved in 25 c.c. of the anhydride, and the solution treated as set out in Table II.

TABLE II.

Estimation of peroxide-oxygen content of benzoyl peroxide in *acetic anhydride* solution under different conditions.

Expt. No.	Amount of sulphuric acid added.	Amount of potassium iodide added. Grms.	Period of standing.	Temp.	Peroxide-oxygen found. Per Cent.
13	none	2 (solid)	10 minutes	Room	6.5
14	"	2 in 2 c.c. water	"	"	6.6
15	"	2 (solid)	1 hour	50° C.	6.3
16	"	"	24 hours	5°–10° C.	6.1
17	1 c.c. 98 per cent.	"	" "	"	nil
18	"	"	1 "	50° C.	nil
19	1 c.c. 50 per cent.	2 in 2 c.c. water	24 "	5°–10° C.	2.5

Theoretical results were obtained by adopting the details already given in the case of glacial acetic acid. The reaction product must, however, in this case be vigorously shaken with water before the titration, since starch solution does not give a blue colour with iodine in the presence of much acetic anhydride.

It will be observed that addition of sulphuric acid, even in small quantity (Expt. 19; cf. Expt. 6), again leads to low results. The explanation of the cause

of this can now be obtained by making the following test-tube experiment, which shows that some or all of the liberated iodine is taken up by the acetic anhydride in the presence of potassium iodide, and that the peroxide itself is not concerned: A crystal of potassium iodide is heated with about 1 c.c. of acetic anhydride and a few drops of concentrated sulphuric acid; iodine is, of course, immediately liberated. The tube is cooled and its contents poured into about 50 c.c. of cold water. The iodine immediately disappears, and the solution does not yield a blue colour with starch, nor does a blue colour appear with addition of (a) more potassium iodide, (b) iodine-free hydriodic acid, (c) acetic acid, or (d) alkali. On addition of a considerable quantity of concentrated sulphuric acid an amorphous yellow precipitate slowly appears, which is very sparingly soluble in water, alcohol and ether. It evolves iodine on being heated or on being treated with concentrated sulphuric acid or chloroform, and it yields reactions for acetates and potassium. The yellow substance has not been analysed, but the conclusion seems justifiable that it is a compound of the type $x(\text{CH}_3\text{CO})_2\text{O} \cdot y\text{KI} \cdot z\text{I}$, indications of the formation of which were obtained by Clover (*Amer. Chem. J.*, 1904, 31, 256).

SUCCINYL PEROXIDE.—To ensure the general applicability of the method to straight-chain compounds some succinyl peroxide, $(\text{COOH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COO})_2$, was prepared by the method of Clover and Houghton (*Amer. Chem. J.*, 1904, 32, 55). The product was recrystallised twice from acetone, dried in a current of warm air, and the peroxide-oxygen content determined in glacial acetic acid solution. No sulphuric acid was added, and the liberated iodine was titrated after shaking for a few minutes with the potassium iodide solution. The result was 6.7 per cent., against a calculated value of 6.8 per cent. Clover and Houghton (*loc. cit.*) obtained 6.7 per cent., using water as solvent.

ALCOHOL, ACETONE, ETC., AS SOLVENTS.—Gelissen and Hermans (*loc. cit.*) estimate benzoyl peroxide by dissolving 0.2 gm. of the sample in 10 c.c. of acetone, adding 3 c.c. of concentrated aqueous solution of potassium iodide, and titrating the liberated iodine immediately with *N*/10 sodium thiosulphate solution. We have confirmed the accuracy of this method, no sulphuric acid being added. Ordinary technical acetone also gives theoretical results (6.6 per cent.), but in this case a blank experiment must also be made. Estimations can also be carried out in solutions in alcohol (both 99 per cent. and 95 per cent.); no blank is required in this case, but a comparatively larger quantity of the solvent (about 100 c.c.) is required for 0.2 gm. of the sample. Ether and carbon tetrachloride are unsatisfactory as solvents for the purpose, both in the cold and on heating.

OXIDISED OIL.—Estimation of the peroxide-oxygen content of a sample of oxidised linseed oil was then examined. The sample was prepared by bubbling oxygen through the oil until the nett increase in weight was 4.03 per cent. Concordant results, namely, 2.2 per cent. of peroxide-oxygen, were obtained by adopting the following procedure: About 1 gm. of the oil is weighed and dissolved in 25 c.c. of glacial acetic acid contained in a glass-stoppered bottle. To the solution are added (i) 1 c.c. of approximately 50 per cent. sulphuric acid ("A-R."), and (ii) 2 c.c. of cold saturated potassium iodide solution ("A-R"). The stopper

of the bottle is wetted with dilute potassium iodide solution. The mixture is then allowed to stand in the dark for 24 hours at room temperature, after which it is diluted with about 100 c.c. of distilled water and titrated with *N*/10 sodium thiosulphate solution. At the same time, in bottles of the same shape and size, the following tests are made:—(i) with a benzoyl peroxide control, and (ii) two blanks.

About 20 experiments were carried out in which the following factors were separately varied: (a) The quantity of sulphuric acid added; (b) the duration of the experiment; (c) the temperature.

(a) If concentrated sulphuric acid is employed the oil undergoes charring and the result is low. If, on the other hand, the acid employed is much below 50 per cent. concentration the oil is partially thrown out of solution, and the result is again low.

(b) If for any reason it becomes necessary to continue the duration of an estimation for more than 24 hours, an oxygen-free atmosphere must be provided, because with long exposures, say 48 hours, the blanks give very discordant figures, although the bottles may be of the same size and shape. This explains also why *two* blanks are recommended, even when the exposure is only 24 hours. The average of the two readings obtained with the blanks is deducted from the titration figure. Some typical readings of the volume of *N*/10 sodium thiosulphate run into the blank mixtures of glacial acetic acid, sulphuric acid and potassium iodide were: (i) 4.25, (ii) 4.35, (iii) 4.45 c.c.

(c) No advantage is gained by keeping the bottles in an ice-box, and discordant figures result by warming in a water-bath to 50° C.

The above modified Fahrion method has been used with success in the examination of a large number of complex compounds of oily and gummy consistency which were obtained by the oxidation of vegetable oils. It should be noted, however, that the method must be used with caution in the case of those substances (*e.g.* raw drying oils) which absorb iodine directly from glacial acetic acid solution, as low results would then be obtained. Direct absorption of iodine by drying oils in this manner is, however, slow, and after 24 hours' contact usually corresponds to an iodine value of approximately 25, as compared with a true iodine value of about 170.

A few values of general interest are set out in the Table below:

TABLE III.

Substance.	Peroxide-oxygen. Per Cent.
1. Linseed oil (heat thickened)*	0.7
2. Do. (blown)*	1.6
3. Wood oil (blown)*	3.4
4. Do. (exposed for 18 months)*	6.3
5. Oxidised glyceride from wood oil† (glyceride of β -elaeostearic acid)	4.5-4.9
6. Portion of (5) insoluble in petroleum spirit†	3.0-3.2

* A correction was made in these cases for the iodine which was absorbed by the oil, by ascertaining separately the effect of addition of the quantity of oil employed in the determination on a benzoyl peroxide blank experiment.

† Morrell and Marks (*loc. cit.*).

SUMMARY.—The effects of various conditions on the determination of the peroxide-oxygen content of organic peroxides have been investigated. Modified conditions have been put forward for the determination of the peroxide-oxygen content of oxidised oils and their decomposition products.

Our thanks are due to Messrs. Mander Bros., Ltd., Wolverhampton, in whose laboratory part of the above work was carried out.

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DISCUSSION.

The PRESIDENT wondered why sulphuric acid was necessary at all in the presence of so much acetic acid, since some of the experiments without sulphuric acid seemed to have given satisfactory results.

Dr. H. E. COX suggested that if iodine were really absorbed by glacial acetic acid, it would be decomposed again on the addition of water.

Mr. J. R. NICHOLLS said that the difficulty in the titration of peroxides was the lag in the liberation of the iodine due to the presence of water. He suggested that in the case of an oil dissolved in a large proportion of solvent, the solvent might be oxidised before the oil.

Mr. S. MARKS, replying, said that with regard to the addition of sulphuric acid—he took it that when sulphuric acid was added potassium iodide was decomposed and the function of the sulphuric acid was to take up the potash. In the case of oils he had certainly found that a small quantity of sulphuric acid (say 1 c.c. of 50 per cent.) was advisable—otherwise one did not get good results. He did not see how one could apply a correction for the absorbed iodine; when one determined an iodine value there was no sulphuric acid, and the two figures were not obtained under the same conditions. The average of the two blanks had been taken in order to avoid the discrepancy obtained in the titration of iodine after the use of glacial acetic acid and a saturated solution of potassium iodide. Answering Dr. Cox, Mr. Marks said that the addition of water did not effect decomposition. With regard to the formation of blue colour, when he failed to get a blue colour he added to the reaction mixture quite a number of substances with a view to “coaxing” it. When iodine had disappeared from view by the addition of water, he found that the blue colour did not appear with potassium iodide, iodine-free hydriodic acid, more acetic acid or more alkali, and he felt that the possibility of iodine being there and not showing was rather remote.

Electrometric Determination of Copper.

I. MÜLLER AND RUDOLPH'S METHOD.

By MARJORIE E. PRING, M.Sc., AND
JAMES F. SPENCER, D.Sc., Ph.D., F.I.C.

GRAVIMETRIC methods of determining copper, with the exception of Rivot's thiocyanate process, are troublesome to carry out, and on occasion may be very inaccurate. Consequently, volumetric methods of determination are usually employed. Difficulties frequently occur in the volumetric determination of copper when highly coloured solutions, or solutions containing other metals have to be used. We have, therefore, investigated the existing volumetric methods for the determination of copper using electrometric methods of ascertaining the end-point of the titration, and, in addition, we have examined several possible new methods in the same way. Electrometric titrations, in addition to other advantages, allow one to carry out determinations in highly coloured and even in turbid solutions, and frequently in the presence of metals other than that being determined.

A considerable amount of work on the electrometric determination of copper has been published, but a careful study of the results obtained by these methods does not suggest an entirely satisfactory process for the electrometric determination of copper.

PRECIPITATION OF INSOLUBLE COPPER COMPOUNDS.—In 1911 Dutroît and von Weise (*J. Chim. Phys.*, 1911, 9, 608) investigated the titration curves obtained during the precipitation of insoluble copper compounds by various reagents. The process as a method for the determination of copper was unsuccessful unless a polarised copper electrode was used. In the case of the precipitation of hydroxide, ferrocyanide, thiosulphate, iodide, phosphate and thiocyanate either a poor end-point was obtained in the titration or the curves were irregular. The only precipitation giving good results was that of the sulphide, but even this did not yield an accurate end-point. The titration of solutions of copper salts was further investigated by Hedrich (*Diss.*, Dresden, 1919), and from his results it may be taken that the method is unsuitable for general use. Oosterheld and Honegger (*Helv. Chim. Acta*, 1919, 2, 238) investigated the electrometric titration of iodine, liberated by the action of potassium iodide on cupric salts, by means of sodium thiosulphate. Their experiments show that a sharp end-point can be obtained, but their work deals mainly with the effect of sulphuric acid of varying concentration on the course and result of the titration.

TITRATION WITH TITANOUS SALTS.—Several accounts have been published of the electrometric determination of copper by titration with solutions of titanous salts. Thus Zintl and Wattenberg (*Ber.*, 1922, 56, 472) add an excess of titanous

chloride to the solution of the copper salt and titrate the excess with either potassium bromate or potassium dichromate. Willard and Fenwick (*J. Amer. Chem. Soc.*, 1923, **45**, 933) in a short note state that solutions of cupric salts may be titrated directly with titanous sulphate with good results if a bimetallic electrode system is used. Tomiček (*Rec. Trav. Chim.*, 1924, **43**, 798) investigated the direct titration with titanous chloride and found that the results were always about 1.0 per cent. too high, but in the presence of potassium iodide or potassium thiocyanate, both of which precipitate the cuprous salt formed in the reaction, good results could be obtained. When tartrates or tartaric acid are present good results can be obtained only in the presence of potassium iodide; the presence of potassium thiocyanate has a disturbing effect on the reaction. Zintl and Rauch (*Z. anorg. Chem.*, 1925, **146**, 281; *Z. Elektrochem.*, 1925, **31**, 428) reinvestigated the indirect method of oxidising the excess of titanous salt with potassium bromate and confirm the previous results of Zintl and Wattenberg. They maintain that the method is very accurate. The high results obtained by Tomiček in the direct titration with titanous chloride are attributed to the presence of dissolved oxygen in the copper sulphate solution. To remove this error they suggest either boiling the solution in an atmosphere of carbon dioxide before titration or adding a few drops of titanous chloride solution and oxidising the excess with potassium bromate or potassium dichromate. Kolthoff, Tomiček and Robinson (*Z. anorg. Chem.*, 1926, **150**, 157), on repeating Tomiček's experiments, find that the results of direct titration are consistently 0.2–1.2 per cent. too high. The best results are obtained when correction is made for the dissolved oxygen, as stated above, but the process is troublesome. The fall in the E.M.F. at the end-point is not very pronounced, and even when the correction for dissolved oxygen is made the accuracy is not great. Further, it is found that the presence of a trace of copper sulphate in the titration of dichromate with titanous chloride raises the titre 0.2 per cent. This point in itself tends to vitiate the results obtained by the indirect method of estimating copper. In a reply to this criticism Zintl (*Z. anorg. Chem.*, 1926, **152**, 35) suggests that Kolthoff, Tomiček and Robinson used unsatisfactory methods to standardise their titanous chloride solution. He again points out the necessity for removing dissolved oxygen from the solution, and he insists that an error of 0.2 per cent. is not greater than the errors in other methods used by these authors. He further states that the method always gives a sharp end-point. The determination of copper by reduction of the cupric salt has also been investigated by Bucherer and Schupp (*Ind. Eng. Chem.*, 1926, **18**, 121). They titrated cupric salts directly with stannous, titanous and chromous chlorides, respectively; also excess of these reagents was added to the cupric salt, and the excess titrated with potassium dichromate solution. Direct titration with stannous chloride and titanous chloride gave high results, whilst that with chromous chloride gave good results if the value taken was the mean of the values calculated from the titrations represented by $\text{Cu}^{2+} \rightarrow \text{Cu}^+$ and $\text{Cu}^+ \rightarrow \text{Cu}$. In those cases where an excess of the reducing agent is added and the excess titrated back with potassium dichromate it was found that good results were obtained with chromous chloride, but with titanous

chloride the values were too high, whilst with stannous chloride the method is impracticable, for both the cuprous compound and the excess of stannous chloride are oxidised. Müller and Adam (*Z. Elektrochem.*, 1923, 29, 49) attempted to determine the concentration of a cupric salt by adding to it an excess of potassium cyanide and titrating the excess with silver nitrate, using a silver electrode. Trustworthy results were not obtained, since the reduction of the cupric compound to a cuprous compound only approaches completion when the solution is submitted to prolonged heating, and this affects the concentration of the potassium cyanide. Müller and Rudolph (*Z. anal. Chem.*, 1923, 63, 103) investigated the method of reducing a solution of a cupric salt by sodium bisulphite, heating to 70° C., and then titrating with potassium thiocyanate, using a copper electrode. They state that this process gives results too low by a constant 0.7 per cent. if the conditions are well controlled.

From what has been said it will be clear that none of the methods proposed for the electrometric determination of copper is generally applicable and reliable.

EXPERIMENTAL.

The titrations described were made by means of an apparatus designed by Spencer (*J. Soc. Chem. Ind.*, 1927, 46, 423T), the voltmeter of which could be read to 0.001 volt. The burettes, flasks and pipettes were carefully calibrated, and the materials used were chemically pure. The copper sulphate solutions were prepared from accurately weighed quantities of A.R. material, and the concentration was confirmed by electrolysis. In all cases the solution was mechanically stirred during the titration.

INVESTIGATION OF MÜLLER AND RUDOLPH'S METHOD.—The determination was first carried out, following exactly the instructions given by Müller and Rudolph (*loc. cit.*). To 10 c.c. of a 0.1 *m* solution of copper sulphate 20 c.c. of a 5 per cent. solution of sodium bisulphite and 70 c.c. of water were added. The solution was heated to 70° C., a copper electrode and a 0.1 *N* calomel electrode inserted, and the hot solution titrated with a 0.1 *N* solution of potassium thiocyanate. The E.M.F. of the cell, $\text{Cu} \mid \text{CuSO}_4 \text{ soln.} \mid 0.1 \text{ N KCl.Hg}_2\text{Cl}_2 \mid \text{Hg}$, was measured one minute after each addition of thiocyanate, and the E.M.F. values plotted as ordinates, against the number of c.c. of titrating liquid added, as abscissae, and a titration curve drawn.

The type of curve obtained is shown in Fig. 1; it will be seen that a rise in the E.M.F. occurs at the end-point, which is sufficiently marked to enable the position to be determined within 0.05 c.c. It was found, however, that the titration is difficult to control, and the results obtained do not agree well. Various factors, including the time taken for the addition of the thiocyanate, the temperature and the amount of bisulphite used, appeared to influence the end-point; consequently each of these factors has been separately investigated. Further, it was found that the sharpest end-point was obtained when the copper electrode consisted of a piece of electrolytic copper which had been washed with dilute nitric acid, followed by distilled water, immediately before use.

Influence of Temperature.—Series of titrations were carried out, as described above, at 65° C., 70° C., and 75° C. A solution of copper sulphate (I) containing

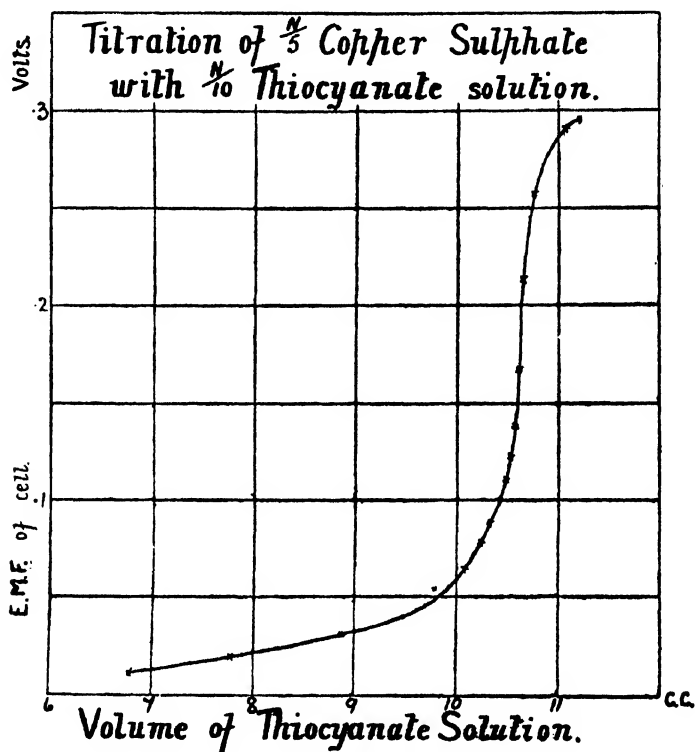


FIG. 1.

24.940 grms. per litre was titrated with 0.1036 *N* potassium thiocyanate solution, which had been standardised against 0.09932 *N* silver nitrate solution.

9·97 c.c. CuSO₄ solution (I) + 20 c.c. NaHSO₃ (5 per cent. solution) + 70 c.c. H₂O

65° C.	70° C.	75° C.
--------	--------	--------

KCNS added. c.c.	E.M.F. Volts.	KCNS added. c.c.	E.M.F. Volts.	KCNS added. c.c.	E.M.F. Volts.
9.00	0.048	9.00	0.050	8.99	0.050
9.24	0.058	9.10	0.059	9.13	0.060
9.35	0.071	9.22	0.068	9.26	0.080
9.46	0.091	9.38	0.095	9.34	0.100
9.58	0.120	9.47	0.115	9.38	0.115
9.62	0.149	9.51	0.128	9.43	0.139
9.66	0.199	9.55	0.140	9.47	0.159
9.70	0.230	9.59	0.178	9.51	0.182
9.74	0.241	9.63	0.218	9.56	0.198
<hr/>		9.67	0.225	<hr/>	
End-point = 9.64		End-point = 9.61		End-point = 9.47	

Theoretically, 9.97 c.c. of copper sulphate solution require 9.61 c.c. of potassium thiocyanate solution. In the case of the titration at 75° C. the solution became brown and turbid before the titration was begun, the end-point was not sharp, and the voltmeter reading was not steady.

A second series of experiments was made with copper sulphate solution (II), which contained 6.336 grms. of copper per litre; this was titrated with 0.0923 *N* potassium thiocyanate solution.

Temperature	..	65° C.	70° C.	75° C.
End-point	..	10.58 c.c.	10.53 c.c.	10.35 c.c.

10 c.c. of CuSO₄ solution (II) require theoretically 10.37 c.c. of 0.0923 N KCNS.

The results show that a small rise in temperature above 70° C. makes a large difference in the results; thus there is a difference of about 1.5 per cent. between the values at 70° C. and 75° C.; on the other hand, the difference between the titre at 65° C. and 70° C. is small, about 0.3 per cent. At temperatures above 75° C. the end-point is difficult to determine, since the change in E.M.F. is small.

Influence of Time.—The effect of changing the time factor was examined, using copper sulphate solution (I). The mixture was prepared as in the previous cases, heated to 70° C., and kept at this temperature for a definite time before commencing the titration. The electrodes were then inserted, and the thiocyanate run in almost to the end-point, which was then found by taking voltmeter readings one minute after the addition of each drop.

9·97 c.c. CuSO ₄ solution (I) + 20 c.c. NaHSO ₃ (5 per cent. solution) + 70 c.c. H ₂ O. Heated for 1 minute.		Heated for 5 minutes.	
KCNS added. c.c.	Voltage.	KCNS added. c.c.	Voltage.
9·00	0·050	9·01	0·054
9·10	0·059	9·29	0·090
9·22	0·068	9·31	0·108
9·38	0·095	9·36	0·121
9·47	0·115	9·40	0·150
9·51	0·128	9·44	0·189
9·55	0·140	9·48	0·219
9·59	0·178	9·52	0·231
9·63	0·218		
9·67	0·225		

End-point 9·61

End-point 9·42

The correct end-point lies at 9.61 c.c. In the case of the solution which has been allowed to stand for 1 minute the solution is green and clear when the titration is begun, and the precipitate is white, whilst the solution kept for 5 minutes at 70° C. is turbid and brown before titration, and the precipitate is slightly coloured. Further, the voltmeter needle drifts in the experiments made with solutions which have been kept for 5 minutes, so that the readings are difficult to take. There is a difference of 1.9 per cent. between the values of the two solutions. A comparison of the titration curves (Fig. 2) will make it clear that the end-point is much sharper for the solution kept the shorter time at 70° C.

Experiments were next made in which the voltmeter was allowed to settle before the reading was recorded and more thiocyanate added. This process was found to be impracticable, for, as the end-point is approached, it was found that

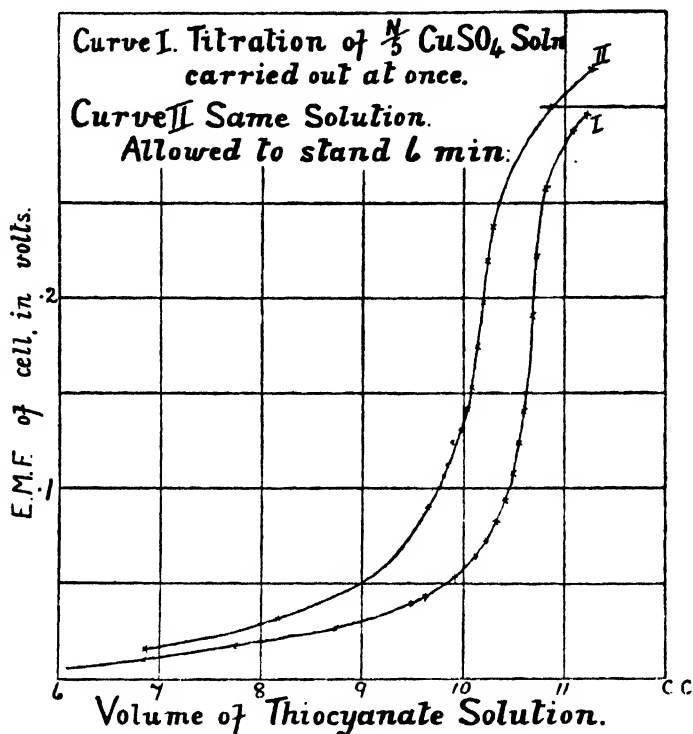


FIG. 2.

after each addition of thiocyanate the E.M.F. rises slowly for a while and then drifts back. Consequently the maximum voltmeter reading was recorded, and the following results obtained at 70°C .

9.97 c.c. CuSO_4 solution (I) + 20 c.c. NaHSO_3 (5 per cent. solution) + 70 c.c. H_2O .

KCNS added. c.c.	Voltage.	KCNS added. c.c.	Voltage.
9.01	0.039	8.99	0.051
9.09	0.048	9.11	0.071
9.24	0.074	9.27	0.091
9.34	0.092	9.37	0.114
9.42	0.118	9.42	0.130
9.46	0.129	9.47	0.145
9.50	0.150	9.51	0.162
9.54	0.170	9.56	0.190
9.58	0.200	9.61	0.211
9.63	0.220	9.67	0.219
9.67	0.232		

End-point 9.56

End-point 9.54

The end-point is poor in this case, and has a value 0.07 c.c., or 0.62 per cent. lower than the correct value, 9.61, obtained by reading the voltmeter one minute after each addition.

Influence of Concentration of Bisulphite.—To examine this point titrations were made with copper sulphate solution (I) at 70° C., using various amounts of

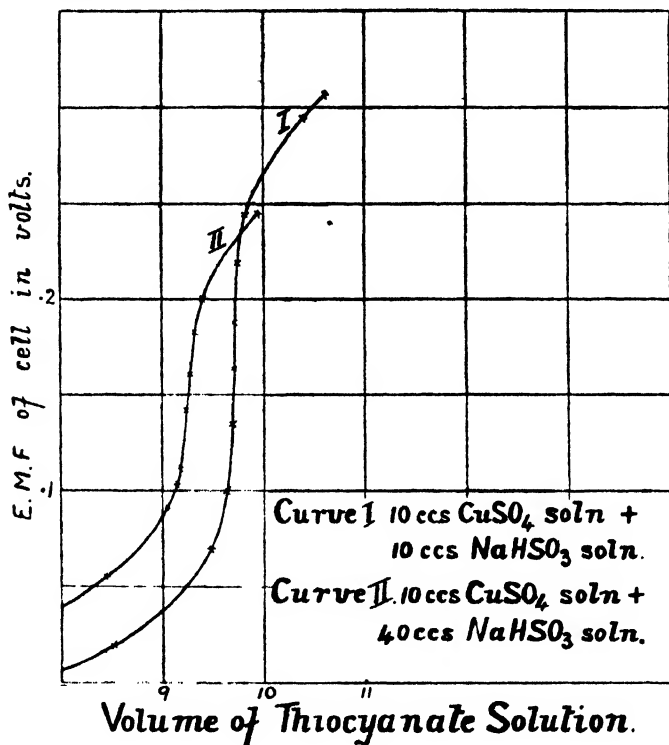


FIG. 3.

bisulphite in 5 per cent. solution, and the total volume was made up to 100 c.c. with distilled water.

9.97 c.c. CuSO_4 solution (I) + NaHSO_3 (5 per cent. solution) + water.

Volume of 5 per cent. NaHSO_3 solution ..	10 c.c.	20 c.c.	40 c.c.
Titration value	9.70 c.c.	9.61 c.c.	9.28 c.c.

The solution was clear and green before the titration was begun, when the lowest concentration of bisulphite was used, and the end-point, as seen in the curves (Fig. 3), is sharp, but it is almost 1.0 per cent. too high, whilst with the most concentrated bisulphite the solution becomes brown and turbid before the titration is begun and the end-point is poor (Fig. 3), whilst the titre is about 3.5 per cent. too low.

DISCUSSION.—The results of this investigation show that Müller and Rudolph's method of electrometric titration of copper is very sensitive to changes of temperature, concentration of bisulphite, and time taken for the operation; hence it

becomes exceedingly difficult to state how far it will furnish accurate results. A comparison of the calculated results with those obtained when the directions of Müller and Rudolph are closely followed gives the following figures.

		Vol. KCNS (calc.). c.c.	Vol. KCNS (exptl.). c.c.
CuSO ₄ solution (I)	..	10.37	10.53
CuSO ₄ solution (II)	..	10.61	10.61

These show clearly that there is no constant error which can be used as a correcting factor, as claimed by Müller and Rudolph. The possibility of obtaining concordant results appears, therefore, to be remote. The results are highest when the temperature is below 70° C., when the solution is titrated as quickly as possible, and when the concentration of the bisulphite is low. Müller and Rudolph attribute their high results to the adsorption of the thiocyanate ion by the precipitate. It appears, however, more probable that they are due to the incomplete reduction of the cupric salt by the bisulphite. In all cases where high results were obtained in the present work the solution was green at the start of the titration and, in consequence, a small quantity of thiocyanate must be used in completing the reduction. When the results are low, that is, when the temperature is above 70° C., or when the solution is kept for a few minutes before the titration is begun, or when a high concentration of bisulphite is used, the solution becomes brown and turbid. In some cases a reddish precipitate is produced, which varies in composition and is evidently the substance described by Chevreul (*Ann. Chim. Phys.*, 1812, (i), **83**, 181). This precipitate contains cupric cuprous sulphite, and its presence in the titration liquid indicates that some of the copper is removed from the solution as sulphite, and consequently that the amount of thiocyanate used must be too low.

A number of experiments were made in which sulphur dioxide was used in place of sodium bisulphite as reducing agent; this prevented the formation of an insoluble complex compound, but the reduction was incomplete, even on boiling. The titration curves show that the end-point is sharpest when the solution does not become turbid before the titration is begun and when the temperature is not allowed to rise above 70° C., but in no case can the process be regarded as satisfactory. The conditions must be exactly regulated to obtain concordant results, and new conditions must be established for varying copper concentrations if reliable results are to be obtained. Consequently the process becomes tedious, time-consuming, and of little practical value.

Acknowledgment is made of a grant from the Department of Scientific and Industrial Research enabling one of us (M.E.P.) to take part in the work.

Apparatus for the Analysis of Small Samples of Gas.

By H. R. AMBLER, B.Sc., A.I.C.

(Read at the Meeting, May 1st, 1929.)

THE simple apparatus here described has been evolved, primarily, for the analysis of samples of gas of about 1 c.c. Samples of this magnitude can be analysed with an accuracy of about 1 per cent.

Where larger samples for analysis are available (*i.e.* 15 c.c.), an accuracy of about 0.1 per cent. is obtainable with a minimum of manipulation.

INTRODUCTION.—In the analysis of samples of gas of about 1 c.c., causes of error become important, which would be quite negligible for larger samples. The chief of these are:—

- (1) Rubber connections, which may lead to (a) small air-locks at the joints, (b) small leaks when the rubber becomes old.
- (2) Physical solution of the constituent gases in each reagent, as distinct from the specific chemical absorption for which the reagent is used.
- (3) The limiting error of reading, which is proportionately greater for smaller samples.

The present apparatus has been designed to reduce such effects to a minimum:

- (1) Rubber connections have been abolished.
- (2) The volume of absorbent reagent has been diminished.
- (3) The sensitiveness of reading has been increased.

APPARATUS AND PROCEDURE.—A diagrammatic sketch of the apparatus is given in Fig. 1.

It consists essentially of two three-way taps, T_1T_2 , connected with the glass bulbs C and B, respectively, and joined together at their "one-way" ends.

The experimental procedure is as follows:

- (1) The gas sample is introduced into the bulb B from A. The way this is done depends on the vessel in which the sample is received. Where possible, it is convenient for this to be fitted with a capillary three-way tap, with the "common" end uppermost. This is joined to A by rubber tubing, and air driven out of the connection with mercury from the apparatus. If, however, as is frequently the case, the sample is contained in an inverted test-tube, it may be transferred to the apparatus by means of a capillary U-tube, one end of which is connected with A by rubber tubing, and the other end, which should be drawn out, inserted under the test-tube in a mercury-jar, after air has been driven out by means of mercury.

(2) The gas sample is transferred to C and measured. This is done by measuring the pressure at which the constant volume of bulb (or bulbs) is filled. The pressure is measured on a mercury manometer, M_1 . By running mercury beyond the tap T_1 , to a marked point F, C is sealed against any leak out of gas or leak in of air during the pressure measurement. It may be convenient, when the highest accuracy is not required, for this point F to be taken on the horizontal part of the tube, instead of on the vertical (water-jacketed) part, as shown in the diagram.

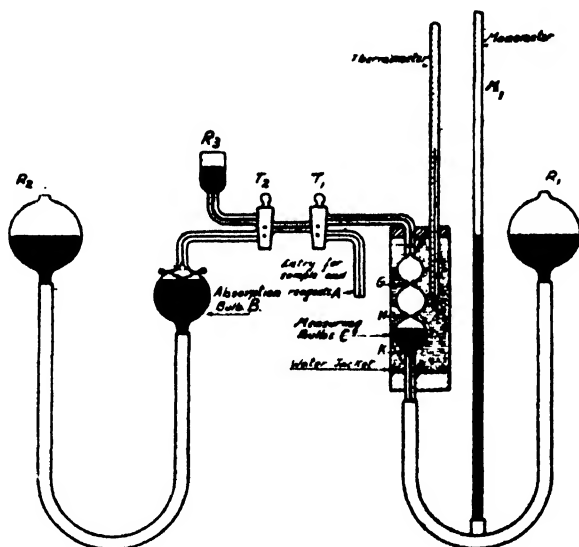


FIG. 1.

(3) A quantity of the appropriate absorbent, equal in volume to about half that of the gas sample, is introduced into B from A.

(4) The gas is transferred to B, where the absorption takes place.

(5) The gas is transferred back to C and again measured. Immediately the gas has passed T_2 the latter is reversed, and the gas followed up by mercury from R_3 to the mark F as before.

The measuring vessel C consists of three bulbs, one, two, or three of which can be used according to the magnitude of the gas sample. In this particular apparatus their volumes are 1, 3 and 6 c.c. respectively. Horizontal marks G, H, K are etched below each bulb. Gas samples, of magnitude ranging from about 0.25 to 15 c.c. (at N.T.P.) can be dealt with. A water jacket fitted with thermometer surrounds the measuring bulbs.

The absorption bulb B is fitted with platinum electrodes and spark gap, or a platinum spiral, or both. The volume of B is about 25 c.c.

The connecting glass tubes are made of capillary tubing of 1 mm. bore.

The manometer is attached to a silver-backed glass scale, 1 metre in length, graduated in mm. This need not be placed inconveniently close to the rest of the apparatus, but may be mounted on a neighbouring wall or other suitable place.

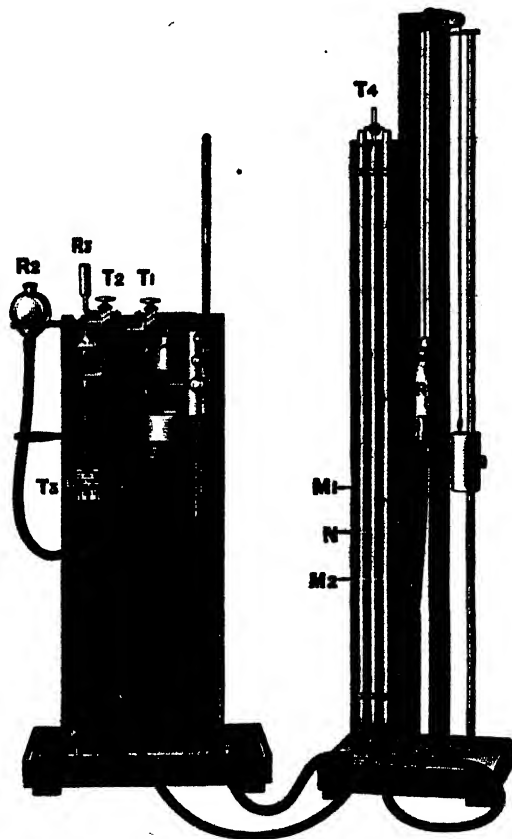


FIG. 2.

The central glass part of the apparatus, with its wooden stand, may then be gently shaken in order to agitate the absorbent solution. Very slight movement gives adequate agitation of the liquid. Reading is very easy and parallax is avoided.

There are none of the difficulties of levelling that are found with the constant-pressure types of apparatus. Manipulation is simple and rapid. A gas of 6 constituents (say CO_2 , O_2 , CO , CH_4 , H_2 , N_2) can be analysed within half an hour.

The size of that part of the apparatus in which the gases are manipulated is quite small, *i.e.* $9'' \times 9'' \times 1''$. It is simple and strong. The amounts of mercury and of reagents are small. The complete apparatus is shown in Fig. 2.

REDUCTION OF ANALYSES.—Let K be the reading on the manometer when the measuring bulbs are filled at atmospheric pressure. This is determined once and for all by connecting them with the atmosphere, through T_1 and T_2 , with R_2 empty, and bringing the mercury to the appropriate mark. (If at any time it is feared that the level of the bulbs relative to the scale can have changed, this can be checked by the same procedure). K is not necessarily level with the mark on the bulb, as the bore of the tube at the mark may not be the same as that of the manometer. By determining K as above, however, capillarity effects are eliminated, provided the bore of the manometer tube is uniform.

Let A be the reading on the manometer at the beginning of the analysis,

Then P , the pressure in the bulbs,

$$= B + A - K, \text{ where } B \text{ is the barometric pressure.}$$

The bulbs are washed out with water between analyses; hence the gas is always saturated with water vapour. The partial pressure of the gas under analysis is then:—

$$B + A - K - W,$$

where W is the vapour pressure of water at the temperature indicated by the thermometer in the water-jacket.

If V be the volume of the bulbs, then the volume of a sample at N.P. is:—

$$V \times \frac{B + A - K - W}{76}$$

If the manometer reading after absorption of, say, CO_2 be A' , the volume of gas at N.P. now is:—

$$V \times \frac{B + A' - K - W}{76}$$

The volume of CO_2 absorbed is, then:—

$$\frac{V(A - A')}{76}$$

The percentage of CO_2 is:—

$$\frac{A - A'}{B + A - K - W} \times 100.$$

The quantity $(B + A - K - W)$, representing the original pressure of the gas sample, is determined once for each analysis. The percentage of each constituent is directly proportional to a difference of readings on the manometer.

BAROMETER ATTACHMENT.—Analysis requires a knowledge of the barometric pressure. A barometer may be incorporated in the apparatus as follows (see Fig. 2). By the side of the manometer, M_1 , is placed a second tube, N , of the same bore, and connected at its lower end with M_1 and R_1 . The upper end is fitted with a capillary tap, T_4 . If R_1 is raised so as to drive mercury past T_4 , the latter closed, and then R_1 lowered to some position lower than T_4 by more than the barometric height, the space below T_4 will be a Torricellian vacuum, and the barometric pressure will be equal to the difference in the heights of mercury in this tube and in M_1 . A barometer reading can be so taken at any time during an analysis. If a drying tube is attached to T_4 , and the latter occasionally left open, the space above the mercury is kept free of water vapour. Normally, the reservoir

is sufficiently high for the barometer tube to be completely filled with mercury. If a leak past T_4 is suspected, R_1 can be raised at any time, and the mercury taken past the tap immediately before reading.

USE OF PRESSURE GAUGE.—It may sometimes be convenient and more speedy, when high accuracy is not required, to read the pressure of the gas on a dial instead of on a mercury manometer. For a portable apparatus this would present considerable advantages.

An atmospheric gauge, has been used in conjunction with the mercury manometer. The gauge was used filled with alcohol, and the level of the mercury and alcohol interface kept constant within very small limits by making its area large, *i.e.* about 50 sq. cm. This was done by causing it to occur in the middle of a large bulb.*

An analysis was carried out, in which readings were taken both on the manometer and on the pressure gauge, and the results from the two sets of readings calculated independently. The figures agreed within 1 per cent. For many purposes, sufficient accuracy could be obtained with the gauge alone.

AUXILIARY MANOMETER.—It is sometimes desirable, particularly in the case of absorptions that take several minutes for completion, to be able to observe the progress of the reaction without having to transfer the gas to and from the measuring bulbs.

For this purpose, an auxiliary manometer M_2 is connected with the absorption bulb B through a three-way tap, T_3 , which, in its normal position, connects B with the reservoir R_2 . If, after gas has been introduced into B, this tap is reversed, it connects B with M_2 and cuts off R_2 . The progress of absorption of gas in the (approximately) constant volume above the absorbing solution in B can then be followed on the manometer M_2 .

PRECAUTIONS IN USE.—As with all types of apparatus, reagents must not be allowed to enter the measuring-bulbs, as their presence in any appreciable quantity may lower the aqueous vapour-pressure in the bulbs.

The portion of capillary tubing between the taps T_1 and T_2 becomes wetted with reagents; it is possible to wash this out between absorptions, by running water from R_2 to A. This is found, however, to be in general unnecessary, since any gas which might thus come in contact with the reagent has already been in contact with the same reagent.

After exploding for hydrogen and methane (and also before a fresh analysis), the absorption bulb should be washed free of alkali. This is conveniently done by washing out once with weak sulphuric acid and then with water, introduced at "A" in the same way as the absorbent reagents, the gas being retained meanwhile in the measuring bulbs. It is advisable at the same time to wash out the measuring bulbs with water, in case any minute traces of alkali had entered them. The washing may be done without loss of gas or admission of air, by drawing a small quantity of water into bulb B, and transferring it to the measuring bulbs in the presence of the gas sample. (If acid has not been washed out of B, some will be carried into the measuring bulbs and may react with traces of carbonates, producing carbon dioxide, affecting the methane figure.) This procedure eliminates

* This would be unnecessary with an all-steel gauge, which could be filled with mercury.

the necessity of a separate washing of the gas with water after absorption of carbon monoxide with ammoniacal cuprous chloride.

For suggestions and useful discussions, I am indebted to Mr. T. Carlton Sutton, M.Sc., with whose approval the apparatus has been developed.

RESEARCH DEPARTMENT,
WOOLWICH.

DISCUSSION.

The PRESIDENT remarked that Mr. Ambler had now taken from the gas analyst the possibility of saying that the sample was too small for analysis. He wished to express his very great appreciation of this paper, particularly of the trouble Mr. Ambler had taken in bringing the apparatus itself to the meeting.

Mr. T. C. SUTTON said that he had been closely concerned with the development of this instrument; such constructive ideas as he had been able to put forward had already been incorporated in it, and he would not detail them here; he had specially welcomed it, since the results of even rapid analyses made with it were accurate, and he could no longer be told that there was "insufficient sample." An analysis to one part in 500 could be made very quickly, and he thought that this, coupled with the fact that this was a simple apparatus which could be kept clean easily, was an important advance in gas analysis. He would like to point out that here was an instrument which, while being as good as any other for the analysis of large samples of gas, could be used without alteration as a sensitive and accurate instrument for micro-analysis. If required, the instrument could be made portable, and so could be taken to mine-heads, etc., when it was necessary to analyse gases on the spot.

Mr. G. N. HUNTLEY said that about 25 years ago he had devised an apparatus which had some resemblance to this one, and it had been described by Travers.

Mr. AMBLER, replying to Mr. Huntley, said that an instrument such as this embodied a number of separate principles; originality was not claimed for each separate part. The present form of the apparatus was the result of extensive adaptations and alterations that had been found useful in his daily work.

A Method for the Separation and Determination of Arsenic.*

BY B. S. EVANS, M.C., Ph.D., F.I.C.

MOST of the methods for the determination of arsenic in metals are based on its distillation as trichloride; the majority of the remainder depend on its precipitation as sulphide; sometimes the two processes are combined. Whilst both of these processes are excellent they have drawbacks, some of which are not always realised. The distillation method, besides the obvious disadvantage of requiring special apparatus, is quite capable of giving low results unless carried out with great caution; it requires the arsenic to be in the reduced condition; where the solution of the sample and distillation of the arsenic are carried out in one operation special solutions are required (*e.g.* strong ferric chloride, calcium chloride and hydrochloric acid solution), which may be exceedingly difficult to prepare free from arsenic, and it is almost impossible also to test the accuracy of these methods; a "blank" is usually involved; in the presence of large amounts of antimony distillation methods become decidedly unsafe unless subsequent separation from antimony in the distillate is resorted to. The sulphide precipitation, at best, is tedious, especially if, as is sometimes recommended, a second precipitation has to be carried out; it is attended also with all the dangers of colloid precipitation, which can be serious, especially among sulphides; it does not lend itself readily to subsequent volumetric determination, a drawback where small amounts are concerned. For the rest, the magnesium pyroarsenate determination is very apt to give low results owing to the solubility of the precipitate, whilst Bettendorf's reagent, though apparently capable of giving good results, requires inordinately long periods of digestion, etc.

PRECIPITATION BY HYPOPHOSPHOROUS ACID.—The precipitation of metallic arsenic by hypophosphorous acid first described by Thiele (*Annalen*, 1890, 263, 361), and applied by Bougault to the determination of cacodylic acid, was the subject of a paper from the analytical point of view by Engel and Bernard (*Compt. rend.*, 1896, 122, 390); this paper was purely academical, and did not deal at all with the problems involved in the separation of arsenic from commercial materials. Brandt in 1913 and 1914 published a series of papers (*Chem. Ztg.*, 1913, 37, 1445, 1471, 1496; 1914, 38, 295, 461, 474) on the application of the method to the determination of arsenic in metals; these papers escaped my notice until after the completion of the present work; moreover, part of Brandt's method and some of his conclusions seem open to criticism, and, in any case, the method does not appear to be used in this country. This paper must therefore be regarded as reopening the subject with fresh data and, to a certain extent, fresh technique. Criticism of Brandt's

* Communication from the Research Department, Woolwich.

method and findings will be reserved till the end. The hypophosphorous acid reduction has much to recommend it from an analytical standpoint.

(a) It has considerable delicacy (0.4 c.c. of $N/100 \text{ As}_4\text{O}_6 = 0.00015 \text{ grm. of As}$), gives a precipitate which is plainly visible on a pulp filter of ordinary size, and which can be determined with exactness.

(b) Carried out as described below, it forms a specific, or almost specific, test for arsenic among the great majority of the commoner elements; it will be shown below, for example, that arsenic can be separated quantitatively with one precipitation from very great excess of the following metals, amongst others:—Iron, copper, lead, chromium, vanadium, manganese, nickel, cobalt, and the alkali metals, and from large excess of tin and antimony by a double precipitation. Messrs. Ridsdale's Standard "White Metal A," for which results are given below, contains small amounts of bismuth and zinc in addition to some of the above-mentioned metals, and they caused no interference. It has been shown, however, that mercury is precipitated as metal (Robinson, *ANALYST*, 1929, **54**, 145). Tungsten also forms an insoluble tungsten blue which masks the reaction.

(c) It is applicable to arsenic in either state of oxidation.

(d) The titration value of the precipitated arsenic as against standard iodine solution is 2.5 times the value it has in the ordinary titration.

METHOD OF DETERMINATION.—The following method was worked out for the determination of arsenic in metals, though it would, of course, be applicable to most substances, as apparently the precipitation is very immune to interference. The points to be borne in mind are the following:

(a) The precipitation must take place in a liquid strongly acid with hydrochloric acid; the reason for this is twofold; firstly, because the arsenic does not precipitate unless hydrochloric acid is present, and not then unless the acid concentration is somewhere about 33 per cent. of strong hydrochloric acid; secondly, because in the absence of hydrochloric acid some other metals, notably copper and bismuth, are precipitated (*cf.* Evans, *ANALYST*, 1922, **47**, 6).

(b) The liquid must be maintained, for some minutes at least, at boiling point and, as precipitation is not immediate and the solution contains a large concentration of hydrochloric acid, it is a wise precaution to carry out the precipitation under a reflux condenser.

(c) Strong oxidising agents should be reduced by boiling with sulphur dioxide, which must subsequently be removed by boiling. Nitric acid must be eliminated by heating with sulphuric acid until fumes appear, or may be destroyed by preliminary treatment with hypophosphite; organic matter must be destroyed by heating with sulphuric and nitric acids.

(d) It has been found that the reduction of certain substances, notably ferric salts, by sodium hypophosphite is apt to be somewhat slow and uncertain, tending toward low arsenic results. The addition of a little cupric sulphate seems

to catalyse this reaction, giving prompt reduction and correct results; as in other cases, possibly owing to the presence of a small amount of iron, the addition of copper has had a beneficial result, the practice has been made of always adding 0.5 grm. of copper in the form of sulphate to the liquid in each determination.

(e) The titration should be carried out as described in the process, for reasons which will be discussed later.

Details of the process as applied to determination of arsenic in various metals are as follows:—

COPPER.—A sample weight of 5 grms. is dissolved in a wide-mouthed beaker (without dilution) in a mixture of 20 c.c. dilute sulphuric acid (1:3) and 10 c.c. of concentrated nitric acid. When solution is complete the cover glass is removed and the liquid evaporated cautiously to dryness on the plate; this operation must be carried out on an asbestos pad, otherwise the liquid "bumps" most violently as soon as any solid separates. When the acid is fuming strongly, and the blue copper sulphate has begun to turn grey, the beaker can be placed on the naked plate and pushed gradually on to the hottest part of it; the cover glass is now replaced, tilted so as to allow escape of the acid fumes, and heating is continued until the drops of nitric acid, which at first collect on the cover-glass, are entirely evaporated. The beaker is now allowed to cool, and the copper sulphate is taken up with 75 c.c. of water; the beaker is then warmed gently until the solid is detached from the glass, and the liquid finally heated to boiling. The contents of the beaker are poured into a 750 c.c. conical flask, and the beaker rinsed in with 75 c.c. of concentrated arsenic-free hydrochloric acid. Two or 3 grms. of sodium hypophosphite are then added and the flask gently warmed until the solution is nearly colourless, if necessary a little more hypophosphite being added; the temperature should not rise above, say, 50° C. When the colour has been discharged thus, 10 grms. of hypophosphite are added, the mouth of the flask closed by a cork carrying a straight tube (approximately 60 cm. long \times 1.5 cm. internal diameter) to act as a reflux condenser, the flask placed on a tripod over a burner, and its contents boiled fairly vigorously for 15 minutes (a rate of boiling such that steam issues gently from the top of the tube is suitable). The solution is next completely cooled, filtered through a pulp filter, and the precipitate washed first with 100 c.c. of dilute (1:3) hydrochloric acid to which 2 or 3 grms. of sodium hypophosphite has been added, finally, thoroughly, 6 or 7 times with 5 per cent. ammonium chloride solution. The filter is transferred to a beaker (tall form 800 c.c. capacity), and the funnel rinsed in with water, a measured excess* of standard iodine is run in from a burette, sufficient titrated water added just to cover the pulp when broken up, and the whole very thoroughly stirred and allowed to stand for about 5 minutes. (The titrated water used in this and the subsequent dilution is obtained by adding starch solution to some distilled water and titrating with *N*/100 iodine until a faint permanent

* An excess of several c.c. at least of *N*/10 or *N*/100 iodine, as the case may be, should be used. With practice, the amount required can readily be judged by the appearance of the precipitate.

blue colour appears). At the end of this time the solution is diluted to about 300 c.c. with titrated water, about 2 grms. of sodium bicarbonate added, and the solution immediately titrated with arsenious oxide solution of the same normality as the iodine used. Only an approximate end-point is obtained, and this not a complete discharge, but only a pronounced lightening of the starch blue colour; an excess of from 1 to 3 c.c. of the arsenic solution is run in, about 2 grms. more of sodium bicarbonate added, and the solution is shaken and allowed to stand until the blue colour is discharged, the liquid is finally back-titrated with iodine, the amount of the latter required being somewhere about the amount of the excess arsenic added; this final titration must be done cautiously, drop by drop, with vigorous shaking, as, if the paper pulp is once stained blue, the stain is not readily removed by the small excess of arsenic remaining; the end-point is sharp. The difference between the total volumes of iodine and arsenic solutions added gives the volume of iodine solution reduced by the precipitated arsenic.

1.0 c.c. of *N*/100 iodine = 0.00015 gm. of As.

The following results were obtained on electrolytic copper to which varying amounts of arsenic had been added.

Copper taken. Grms.	Arsenic added.		Titration. c.c.	Arsenic added. Per Cent.	Arsenic found. Per Cent.
	c.c.	Grms.			
5.0	1.0 <i>N</i> /100	0.000375	2.65 <i>N</i> /100	0.0075	0.0079
5.0	2.0 <i>N</i> /100	0.00075	4.60 <i>N</i> /100	0.015	0.014
5.0	10.0 <i>N</i> /100	0.00375	2.60 <i>N</i> /10	0.075	0.078
5.0	5.0 <i>N</i> /10	0.01875	12.25 <i>N</i> /10	0.375	0.368
5.0	7.0 <i>N</i> /10	0.02625	17.20 <i>N</i> /10	0.525	0.516
5.0	7.0 <i>N</i> /10	0.02625	17.40 <i>N</i> /10	0.525	0.522

BRONZE.—It has been pointed out by S. G. Clarke (ANALYST, 1928, 53, 377) that arsenic cannot be precipitated quantitatively from a stannic chloride solution by means of hypophosphite, owing to the precipitated arsenic reducing the tin to the stannous condition. It was found possible to eliminate this difficulty by the addition of a small amount of hydrofluoric acid; under these conditions, however, it was found that high results were obtained, due, apparently, to the co-precipitation of tin with the arsenic; consequently, the first precipitate was dissolved and re-precipitated, correct results being thus obtained.

The process is carried out exactly as described for copper up to the point where the liquid resulting from taking up the "fumed off" solid with 75 c.c. of water has been transferred to the precipitation flask and rinsed in with 75 c.c. of hydrochloric acid; 10 drops of hydrofluoric acid are then added, followed by 2 or 3 grms. of sodium hypophosphite; the flask is gently warmed until the copper has been reduced, 10 grms. more of hypophosphite are added, and the solution is boiled for 15 minutes under the reflux condenser. The liquid is cooled, filtered through a pulp filter, and washed as described for copper; the funnel is then transferred to a

clean flask, and the arsenic dissolved by treating the filter with 50 c.c. of dilute (1:1) hydrochloric acid to which a few drops of bromine have been added. The filter is washed with 100 c.c. of dilute (1:1) hydrochloric acid, 2 or 3 grms. of hypophosphite are added, and the flask gently warmed until the yellow colour of the bromine has been practically discharged; 10 grms. of hypophosphite are then added, and the arsenic re-precipitated by boiling for 15 minutes under the reflux condenser. The precipitate thus obtained is treated exactly as described for that obtained from copper.

The following results were obtained from test samples of pure copper and pure tin to which varying amounts of arsenic had been added:

Copper taken. Grms.	Tin taken. Grm.	Arsenic added.		Titration. c.c.	Arsenic added. Per Cent.	Arsenic found. Per Cent.
		c.c.	Grm.			
4.95	0.05	4.0 N/100	0.00150	11.1 N/100	0.030	0.033
4.95	0.05	2.0 N/100	0.00075	4.6 N/100	0.015	0.014
4.50	0.50	2.0 N/100	0.00075	5.0 N/100	0.015	0.015
4.50	0.50	4.0 N/100	0.00150	8.9 N/100	0.030	0.027
4.50	0.50	10.0 N/100	0.00375	25.1 N/100	0.075	0.075
4.50	0.50	2.0 N/10	0.00750	5.2 N/10	0.150	0.156
4.50	0.50	4.0 N/10	0.01500	9.9 N/10	0.300	0.297
4.50	0.50	5.5 N/10	0.02052	13.6 N/10	0.411	0.408
4.50	0.50	7.0 N/10	0.02625	17.0 N/10	0.525	0.510

PLAIN CARBON STEEL.—Two points require notice with regard to the application of the method to plain carbon steels.

(a) As mentioned above, the reduction of ferric salts by hypophosphorous acid is apt to be slow and uncertain; the addition of a small amount of copper obviates this difficulty.

(b) The insoluble carbon in the sample may react with the iodine in the titration, giving high results; this difficulty is overcome by oxidation with potassium permanganate and subsequent reduction with sulphur dioxide of the manganese dioxide formed.

To a 5.0 gm. portion of the sample 0.5 gm. of electrolytic copper is added, the whole is dissolved in 30 c.c. of dilute (1:3) sulphuric acid and 15 c.c. of concentrated nitric acid, and any insoluble carbon, etc., filtered off. To the solution 30 drops of a saturated solution of potassium permanganate are added, and the liquid is boiled for five minutes; a few c.c. of a solution of sulphur dioxide are then added, and the liquid is evaporated to dryness (this may be done on the naked plate) and heated till nitric acid is completely dispelled, as described for copper. From this point forward the process described for copper is followed, except that 12 grms. of hypophosphite are used, and the preliminary warming with 2 grms. of hypophosphite is omitted.

The following results were obtained with electrolytic iron to which varying amounts of arsenic had been added:

Iron taken. Grms.	Arsenic added.		Titration.		Arsenic added. Per Cent.	Arsenic found. Per Cent.
	c.c.	= Grm.	Total. c.c.	Net. c.c.		
5.0	Blank		0.3 N/100			
5.0	1.0 N/100	0.00037	2.5 N/100	2.2 N/100	0.0075	0.0066
5.0	3.0 N/100	0.00112	7.5 N/100	7.2 N/100	0.0225	0.0216
5.0	5.0 N/100	0.00188	12.4 N/100	12.1 N/100	0.0375	0.0363
5.0	7.0 N/100	0.00262	17.5 N/100	17.2 N/100	0.0525	0.0516

ALLOY STEELS.—Determinations of arsenic were made in the presence of various metals which may occur in alloy steels, the amount taken being more than the maximum likely to occur in a 5 gm. portion of an alloy steel. The determinations were carried out exactly as for 5 grms. of steel, 0.5 grms. of copper being added to each. The following results were obtained:

Metal taken.	Weight. Grms.	Arsenic added.		Titration.		Arsenic recovered. Grm.
		c.c.	= Grm.	Total. c.c.	Net. c.c.	
Nickel	5.0	Blank		1.1 N/100		
"	5.0	1.0 N/100	0.00037	4.5 N/100	3.4 N/100	0.00051
"	5.0	3.0 N/100	0.00112	8.7 N/100	7.6 N/100	0.00114
"	5.0	5.0 N/100	0.00188	13.3 N/100	12.2 N/100	0.00183
Cobalt	0.5	Blank		1.0 N/100		
"	0.5	1.0 N/100	0.00037	3.0 N/100	2.0 N/100	0.00030
"	0.5	3.0 N/100	0.00112	8.2 N/100	7.2 N/100	0.00108
"	0.5	5.0 N/100	0.00188	13.2 N/100	12.2 N/100	0.00183
Chromium	1.0	Blank		0.5 N/100		
"	1.0	1.0 N/100	0.00037	2.1 N/100	1.6 N/100	0.00025
"	1.0	3.0 N/100	0.00112	6.7 N/100	6.2 N/100	0.00094
"	1.0	5.0 N/100	0.00188	12.0 N/100	11.5 N/100	0.00173
Molybdenum	0.5	Blank		1.1 N/100		
"	0.5	1.0 N/100	0.00037	2.9 N/100	1.8 N/100	0.00028
"	0.5	3.0 N/100	0.00112	7.6 N/100	6.5 N/100	0.00098
"	0.5	5.0 N/100	0.00188	12.1 N/100	11.0 N/100	0.00166

Trials made with tungsten by the above process broke down hopelessly, owing to the fact that the hypophosphorous acid reacts with the tungstic acid to form a dark blue insoluble compound, presumably a lower oxide, which renders any iodine titration impossible. As it was found that a large excess of phosphoric acid takes the tungstic acid into solution and apparently prevents its reduction by hypophosphorous acid, trials were made on 1.8 (=1.0 gm. of tungsten) gm. portions of sodium tungstate to which varying proportions of arsenic had been added. Each sample was dissolved in 65 c.c. of water, 10 c.c. of dilute (1:3) sulphuric acid, 0.5 gm. of copper in the form of sulphate and 20 c.c. of syrupy

phosphoric acid were added, and the liquid was warmed till it was bright; 75 c.c. of hydrochloric acid and 12 grms. of hypophosphite were then added, and the solution was boiled for 15 minutes under a reflux condenser and finished as usual. The following results were obtained:

Tungsten taken. Grms.	Arsenic added.		Titration.		Arsenic recovered. Grm.
	c.c.	= Grm.	Total. c.c.	Net. c.c.	
1.0	Blank		0.5 N/100		
1.0	1.0 N/100	0.00037	2.5 N/100	2.0 N/100	0.00030
1.0	3.0 N/100	0.00112	6.8 N/100	6.3 N/100	0.00095
1.0	5.0 N/100	0.00188	12.0 N/100	11.5 N/100	0.00173

Attempts made, however, to apply this modification of the original method to steels containing high tungsten and high chromium were still unavailing, as such steels, when heated with sulphuric acid until fumes appeared, formed a pasty mass which entirely refused to go into solution again. The only alternative to the evaporation with sulphuric acid seemed to be the removal of the nitric acid by chemical means; this was ultimately accomplished by a preliminary reduction with sodium hypophosphite. The following process was worked out for tungsten steels and any that are rendered insoluble by heating with sulphuric acid until fumes appear; it can, if preferred, be applied to all steels:

A 5 gm. sample of the steel, together with 0.5 gm. of electrolytic copper, is dissolved in 30 c.c. of dilute (1:3) sulphuric acid, 15 c.c. concentrated nitric acid and 20 c.c. hydrochloric acid; 30 drops of a saturated solution of potassium permanganate are added to the liquid, which is then boiled for five minutes, after which 10 c.c. of a saturated solution of sulphur dioxide in water are added, the liquid again boiled for 2 or 3 minutes, 40 c.c. of syrupy phosphoric acid and 40 c.c. of water are added, and the liquid is boiled down to about 70 or 80 c.c. The solution is cooled, roughly measured (if less than 80 c.c. it should be made up to that volume); it is poured into a flask and an equal volume of hydrochloric acid is added and 40 c.c. of water. (This can be used to rinse in the measuring tube and beaker). About 2 grms. of sodium hypophosphite are next added, and the flask is warmed until a brisk effervescence takes place; it is then removed from the plate and sodium hypophosphite cautiously added in about 2 gm. quantities until the nitric acid is practically all dispelled, this point being indicated by the sudden cessation of the violent effervescence when more hypophosphite is dropped in. About 10 drops of hydrofluoric acid are now added, followed by 12 grms. of sodium hypophosphite; the liquid is boiled (fairly vigorously) under a reflux condenser for 15 minutes and finished as usual. In the absence of tungsten the addition of the 40 c.c. of phosphoric acid and 40 c.c. of water, also the treatment with hydrofluoric acid and the use of hydrochloric acid in the initial solution, should be omitted, and the liquid should be filtered after solution.

The following results were obtained with a synthetic mixture representing a

steel containing: Iron, 54; tungsten, 20; chromium, 20; cobalt, 5; and molybdenum, 1 per cent., to which varying amounts of arsenic had been added:

Steel taken. Grm.	Arsenic added.			Titration.		Arsenic added. Per Cent.	Arsenic found. Per Cent.
	c.c.	=	Grm.	Total. c.c.	Net. c.c.		
5.0	Blank			3.4	N/100		
5.0	1.0	N/100	0.00037	5.5	N/100	0.0075	0.0063
5.0	3.0	N/100	0.00112	12.0	N/100	0.023	0.026
5.0	5.0	N/100	0.00188	16.6	N/100	0.038	0.040

BRITISH CHEMICAL STANDARD STEELS.—The arsenic in a number of British Chemical Standard steels was determined by the methods described above, the last described method being only used in the case of steel W. The following results were obtained:

Results were obtained.			Results obtained by hypophosphite process. Per Cent.	
Standard.	Nature of steel.	Results given on certificate. Per Cent.		
A. 2.	Mild steel	0.026 0.032 0.026 0.037 0.036 0.023 0.034	Distillation and titration with iodine. As ₂ S ₃ pptd. in distillate converted into Ag ₃ AsO ₄ in NaC ₂ H ₃ O ₂ solution. Dissolved in dilute HNO ₃ and titrated with KCNS.	0.0370 0.0367
N. 1.	Carbon steel, Mn, 0.53; Ni, 0.26	0.05 0.030 0.022 trace 0.03 0.047 0.020 0.020	Methods not given.	0.0315 0.0297
O. 1.	Carbon steel, Mn, 0.62; Ni, 0.16; Si, 0.16	0.038 0.018 0.019 0.027 0.023 0.024 0.025 0.02	Distillation and iodine titration. As ₂ S ₃ sepn. and iodine titration. Weighed as As ₂ S ₃ and Mg ₃ As ₂ O ₇ .	0.0309 0.0312

Standard.	Nature of steel.	Results given on certificate.		Results obtained by hypophosphite process.
		Per Cent.		Per Cent.
A.	Haematite cast iron	0.040	Distillation and iodine titration.	
		0.042		0.0576
		0.045		0.0573
		0.041		
		0.036	Soln. in HCl, passing evolved gas through Br water.	
		0.053	Solution in HNO ₃ and reduction (<i>J. Iron & Steel Inst.</i> , 1895, i, 114).	
V.	Chrome vanadium steel, Mn, 0.54; Si, 0.16; Cr, 0.86; V, 0.27	0.016	No method given.	0.0132
		0.015		
		0.016		
B. 4.	Carbon steel, Mn, 0.73; Si, 0.03	0.138	Distillation.	
		0.138		0.162
		0.142		0.162
		0.145		0.168
		0.140		
		0.140		
W.	Chrome vanadium tungsten cobalt steel	0.01	Process not given.	0.016

These figures are of no value for the purpose of establishing the process, but they are of considerable value as a criticism of the presumably best methods available hitherto; the variation of the referee analysts among themselves (in one case (N. 1) amounting to, at least 100 per cent.) showing that all is not well with the processes used. The case of B.4 is significant. The referees' figures agree fairly closely, but the results of three closely agreeing hypophosphite determinations come 0.02 per cent. higher; examination of the figures given in this paper will show that the latter process tends to give low results rather than high. Two independent determinations by Ibbotson's method gave 0.160 and 0.167 per cent. It would seem that the distillation method may give very low results.

SIGNIFICANCE OF THE "BLANK."—The term "Blank" occurring in the various tables refers to actual arsenic in the materials (iron, nickel, etc.) used as a basis for the experiments. The reagents used appeared to be substantially free from arsenic; the arsenic was in all cases visible as a brown precipitate of about the right amount on the filter pulp; thus the term is not used in the sense of iodine adsorbed on the filter pulp or any similar gain in apparent arsenic. Some experiments made throw an interesting light on the latter question. In the process originally tried the titration was carried out in the following manner:—The filter and precipitate

were stirred with an excess of standard iodine solution, sodium bicarbonate was added, and an amount of standard arsenic exactly equivalent to the iodine added was run in; titration with standard iodine should now give an exact measure of the arsenic precipitate. For small amounts of arsenic (indeed down to quite low amounts) this was found to be the case, results of surprising accuracy being obtained; for high amounts of arsenic, however, low results were found, and the higher the amount the greater the relative loss, whilst below a certain limiting amount of arsenic results were high. It has been stated that filter pulp stirred up with iodine removes some of the iodine and that this is due to reducing substances in the pulp; suggestions have been made for preliminary treatment of the pulp with oxidising agents to remove these substances. In view of the accuracy with which small amounts of arsenic could be determined by this method, the existence of this blank seemed improbable; on determining the blank however a considerable one was found, amounting indeed to 1.0 c.c., an amount which if applied would have vitiated every one of the considerable number of accurate determinations which had been made. A blank carried out on pulp which had been treated with a solution of bromine in dilute hydrochloric acid gave substantially the same result, as also did one on asbestos pulp; it was, however, noted that the pulp always remained tinged with blue after the arsenic solution had been added, showing that iodine remained adsorbed on the pulp, although the solutions always required an excess of iodine and gave a clear end-point. A blank was therefore carried out with ordinary untreated pulp. Ten c.c. of *N*/100 iodine were added, and the mixture stirred, and 2 or 3 grms. of sodium bicarbonate were added, followed immediately by 15 c.c. of *N*/100 arsenious oxide solution; the beaker was allowed to stand for a few minutes, and the liquid was then titrated with *N*/100 iodine solution; the amount required was 5.0 c.c., the exact equivalent of the excess of arsenic added. The various results obtained are shown below:

	Excess of <i>N</i> /100 I required. c.c.
(a) Pulp filter stirred with 10 c.c. of <i>N</i> /100 I; back-titrated with 10 c.c. of <i>N</i> /100 As_2O_3	1.0
(b) Pulp treated with Br, HCl and washed; then as (a)	0.9
(c) Asbestos as (a)	0.8
(d) Pulp stirred with 10 c.c. of <i>N</i> /100 I; back-titrated with 15 c.c. of <i>N</i> /100 As_2O_3 ; re-titrated with <i>N</i> /100 I	no excess

The anomaly of getting accurate results on small amounts of arsenic, in spite of the existence of a relatively large blank when arsenic is not present, is therefore explained. When a certain amount of precipitated arsenic is present some of the added iodine is used up, so that the arsenic subsequently added is sufficient to extract the iodine adsorbed on the pulp; when no precipitated arsenic is present the amount of arsenic added, though sufficient to reduce the iodine, will not remove it from the pulp; hence there is in the solution an excess of arsenic which will combine with an excess of iodine. With very low amounts of arsenic the blank comes partially into operation, giving high results; with high amounts of arsenic

there is a large excess of the latter in the solution which, in its turn being adsorbed on the pulp, gives low results. The method of titration described avoids these various errors. Another source of error was found in the fact that the distilled water in use would reduce an appreciable amount of iodine; this was eliminated by adding starch to the distilled water to be used for diluting the liquid prior to titration and adding $N/100$ iodine, drop by drop, until a blue tinge appeared.

"WHITE METAL A" STANDARD.—A determination was made by the hypophosphite method of arsenic in the "White metal A" Standard of the British Chemical Standards series. The standard has the following composition:—Lead, 82.6; antimony, 12.04; tin, 4.64; copper, 0.33; iron, 0.06; bismuth, 0.03; arsenic, 0.06; zinc, 0.08 per cent.; it therefore presented certain difficulties for determination of arsenic by the usual methods, which difficulties are reflected in the diversity of the methods used by the referees. Details of the process used are as follows:—A 5 grm. sample was dissolved in a mixture of 20 c.c. of nitric acid, 100 c.c. of water, 30 c.c. of a solution of citric acid (100 grms. in 200 c.c. of water), the solution boiled and filtered, and the precipitate washed with hot water, both filtrate and precipitate being retained. The filtrate was precipitated with 20 c.c. of dilute (1:3) sulphuric acid, the precipitate filtered off and washed with 2 per cent. sulphuric acid, and the filtrate evaporated until the sulphuric acid fumed strongly, the citric acid being destroyed by repeated additions of nitric acid. The residue was taken up with 75 c.c. of water and poured into a flask, and the beaker rinsed in with 75 c.c. of hydrochloric acid; the precipitate retained from the initial filtration was dissolved and washed through into the same flask with 100 c.c. of dilute (1:1) hydrochloric acid in repeated small quantities. To the solution in the flask 1 c.c. of hydrofluoric acid and 10 grms. of sodium hypophosphite were added; the solution was boiled for 15 minutes under a reflux condenser tube, and the precipitated arsenic, after filtering and washing as usual, was re-dissolved and re-precipitated and finished as described under bronze. The amount of arsenic thus found was 0.059 per cent.; the results of the referees' determinations, by a variety of methods, as given on the certificate were:—0.06, 0.08, 0.08, 0.04, 0.05, 0.06, 0.05, 0.05, 0.04, and 0.05 per cent.

ARSENICAL PYRITES.—Some determinations were carried out on a sample of arsenical pyrites supplied by a well-known analyst who certified the arsenical content to be 0.325 per cent.; the method used was that described for tungsten steels, omitting the use of hydrochloric acid in the initial solution and the subsequent addition of phosphoric and hydrofluoric acids. The following results were obtained:—0.339, 0.338, 0.338, 0.346 per cent.

It will be noted that the above figures, whilst being higher than that found by the donor of the sample, differ also somewhat widely amongst themselves; the sample was not very finely divided, and segregation of the arsenic is undoubtedly the explanation. Moreover, the sample was several years old, and changes may have taken place, rendering the difference from the original determination more apparent than real.

In all precipitations of arsenic with hypophosphorous acid care must be taken to keep up the concentration of hydrochloric acid; if this drops much below 33 per cent. (of the concentrated acid) the arsenic fails to precipitate, and it will be noted that the present work uniformly employs a strength of 50 per cent.; it follows from this that any washing, rinsing, etc., that may be necessary prior to precipitation and after the hydrochloric acid has been added must be done with 50 per cent. hydrochloric acid and not with water. It looks as though the reaction of arsenic salts with hypophosphorous acid involved the un-ionised trichloride and not the As''' ions.

ENGEL AND BERNARD'S METHOD.—The method published by Engel and Bernard (*loc. cit.*) is identical in principal with that advocated in this paper; they, however, introduce details, *e.g.* a digestion of 12 hours, which vastly increase the time required without increasing the accuracy; their process, too, is only concerned with the determination of arsenic, and is not worked out for its application to technical analysis.

BRANDT'S METHOD.—Brandt's process (*loc. cit.*) deals with the application of the method to ore and metal analysis. He finds that there is no loss on boiling during precipitation and does not even use a reflux condenser; this agrees with my experience; he works with a volume of 60–100 c.c. (which contains 30 to 35 c.c. of concentrated hydrochloric acid) and uses 15 grms. of hypophosphite; after adding the hypophosphite he allows the liquid to digest hot for half-an-hour and boils for 15 minutes; the present work shows the digestion to be unnecessary. With regard to titration he uses two methods (a) Engel and Bernard's original titration, in which an amount of iodine just sufficient to dissolve the arsenic is added, which converts the arsenic into the trivalent state, then sodium bicarbonate, finally further iodine until the starch reaction is obtained, the arsenic then being in the pentavalent state. This procedure appears to be sound though slow, but I do not agree with Brandt's suggestion that in case of over-titration (which appears to be easy) thiosulphate should be used for back-titration; a somewhat extensive comparison of this reagent with arsenious oxide showed that the latter was the better; in $N/100$ solution infinitely so. (b) Brandt's alternative method of titration depends on the fact that, when arsenic dissolves in iodine, acid (hydriodic and arsenic) is produced which can be used to liberate iodine from a mixture of iodide and iodate; in all, 6 atoms are liberated and 5 are reduced by the arsenic; hence $\text{As} = \text{I}$. This method, ingenious as it is, is completely discounted by the fact that, apart from various corrections apparently needed, 1 c.c. of standard iodine corresponds to five times the amount of arsenic that it does in either Engel and Bernard's method or in that of the present paper.

In his method for steel Brandt makes the statement that a high manganese content tends to cause the distillation method to give low results; similarly, the practice of neutralising the distillate with sodium hydroxide; this may account for the disagreements noted earlier. His method of determination of arsenic in steel seems open to criticism on one or two points: he dissolves the sample in dilute

hydrochloric acid and potassium chlorate and boils the solution down to a convenient bulk before adding the rest of the hydrochloric acid and hypophosphite; this procedure was challenged by Andrews (*Chem. Ztg.*, 1914, 295) as liable to cause loss of arsenic by volatilisation; Brandt replied that the arsenic was not lost, the concentration of hydrochloric acid being kept low. Granted that the arsenic is retained, the real explanation probably is that the arsenic is kept in the less volatile pentavalent condition; the present method renders such volatilisation impossible. As he has not added any copper Brandt relies on a rather excessive amount (40 grms. per 10 grms. of Fe) of hypophosphite for the reduction of the iron; this reduction is apt to be slow and uncertain, but the addition of a small amount of copper makes it complete and almost instantaneous. One criticism to be made of Brandt's work has to do with his plan of experimental proof; he shows that the arsenic can be separated from individual metals, he does not show that it can be separated from a complicated mixture like a modern steel; the present work shows that (e.g. when high chromium, high tungsten are present in a steel) this may be an unjustifiable assumption. In dealing with steel he makes no mention (*inter alia*) of tungsten; it is quite certain that his method would break down in presence of this element.

A bad feature of his method as a whole is the practice of washing the arsenic precipitate with hot water; leaving out of consideration the statement that the precipitate is easily oxidised (which Brandt denies), he frequently attempts to wash the precipitate free from a substance which is easily oxidised itself, and when oxidised is liable to attack the arsenic (e.g. FeCl_2 or Cu_2Cl_2), or from a strong reducing agent which is insoluble in hot water (e.g. Cu_2Cl_2) and is liable to reduce iodine. This probably accounts for his statement that copper is apt to co-precipitate with arsenic, and, moreover, prevents its complete precipitation; as shown earlier, copper exerts no deleterious action whatever. On the other hand, some of the initial work for this paper seemed to show a tendency for arsenic to dissolve slightly in water; this tendency is not uncommon in precipitated metals and was countered by the addition of ammonium chloride.

With regard to his separation from tin his results are incomprehensible. S. G. Clarke has found (*loc. cit.*) that arsenic cannot be precipitated from a hydrochloric acid solution containing a large amount of tin, and I can amply confirm that statement.

No work has been done on bismuth for this paper, but Brandt's assertion that good results can be obtained from a single precipitation, taken in conjunction with his statement that bismuth itself precipitates in weak hydrochloric acid and redissolves when more acid is added, appears dubious; every condition for co-precipitation appears to be present.

Official Appointments.

THE Minister of Health has confirmed the following appointments:—

Mr. ERIC VOELCKER, A.R.C.S.I., F.I.C., as Additional Public Analyst for the County of Buckingham (August 7, 1929) and as Additional Public Analyst for the County of Oxford (August 17, 1929).

Mr. RHYS P. CHARLES, F.I.C., as Agricultural Analyst for the County Borough of Merthyr Tydfil (August 13, 1929).

Mr. H. G. MONK, B.Sc., F.I.C., as Agricultural Analyst for the County Borough of Salford (August, 1929).

Notes.

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

OCCURRENCE OF THE TETANUS BACILLUS IN CANNED PEAS.

MANY cans in a consignment of imported canned peas were found, on arrival in this country (Persia) during the hot season, to be "blown," and the cause was made the subject of a special investigation.

The contents had a most putrid odour; the covering liquid was turbid, and particles of stalk and leaves were generously admixed with the peas.

Examination of the internal surface of a large number of cans, which were of the "sanitary" type, revealed a general and uniform dullness of the tin coating; in the vicinity of the seams there had been more intense action and the iron-plate had been exposed in a number of fine, hair-like lines. Only a trace of iron was found in the contents of each of the four cans examined chemically, but the quantity of tin which had been removed from the containers was abnormally high for this type of canned vegetable, especially so since the consignment, as far as we were able to discover, was from a recent packing. The weight of the contents of each can was approximately 400 grms., and the quantities of tin present in the peas and liquor were 0.83, 0.79, 0.74, and 1.10 grains of tin per lb., respectively.

The gas from the headspaces of four cans was collected and examined in a Bone and Wheeler apparatus, with results as below:—

Can No.	1.	2.	3.	4.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Carbon dioxide	42.3	44.0	53.6	58.2
Oxygen	0.2	0.4	Nil	0.4
Hydrogen	0.8	0.4	Nil	0.8
Nitrogen (by difference)	56.7	55.2	46.4	40.6

For the bacteriological examination two c.c. of liquor were removed from a can, with the usual aseptic precautions, one c.c. being added to each of two

Robertson's bullock's heart media tubes. This procedure was adopted for each of three other selected cans, and four tubes were incubated anaerobically at room temperature (92°–98° F.) in a Laidlaw's jar for 3 days. The remaining tubes, one from each can, were incubated at 37° C. for the same period. The results of the examination have been tabulated as follows :—

Tubes.	A.	B.	C.	D.
Aerobic. 37° C. 72 hours.	Thick reddish film on broth. <i>B. subtilis</i> <i>B. mycoides</i> . Gram-negative bacilli. No spores.	Cloudy broth. No film. Gram-positive bacilli in chains. No spores.	Thick reddish film on broth. Gram-negative bacilli. No spores.	Cloudy broth. No film. Gram-positive bacilli. Mycoides type.
Anaerobic. Room temperature. 72 hours.	Deep red film on broth. <i>B. subtilis</i> . <i>B. mycoides</i> . Many spores.	Cloudy broth. No film. Gram-positive bacilli in chains.	Cloudy broth. No film. Gram-positive bacilli. Mycoides type. No spores.	Clear broth. No film. Scanty gram-positive bacilli.

Anaerobic incubation was continued for a further period of four days, at the end of which time the culture in tube C showed typical *B. tetani*. A few Gram-negative bacilli were contained in the tubes A and D.

One c.c. of the broth from the tube C was injected subcutaneously into a three-quarter grown male white rat, which was examined at the end of three and four hours after inoculation. On each occasion the animal appeared to be very ill, its hind legs were partially paralysed, and its back stiffly arched. Although careful watch was made, no typical spasms were seen on these occasions. At the end of 7½ hours the rat was found dead in a hard spasm.

Attempts were made to isolate the *B. tetani* in pure culture in order to study its immunological properties in more detail. The method of Fildes was used, but after twelve attempts it was abandoned.

Further experiments were made with ten-day anaerobic broth cultures of the mixed culture, filtered through an earthenware candle, and with the addition of a living culture of *Staphylococcus aureus*. The sterile filtrate was injected into two rats, one of which was protected with antitoxin. No ill-effects were noticeable. The strain of *tetanus* appeared to lose virulence after sub-culturing, and though both filtered and unfiltered cultures of the bacillus were injected into rats, no further evidence of toxicity was obtained.

F. MARSH.
J. HENDERSON.

ANGLO-PERSIAN OIL CO., LTD.,
PERSIAN GULF.

THE DETERMINATION OF FORMALDEHYDE IN CERTAIN PHARMACEUTICAL PREPARATIONS.

ATTEMPTS to determine formaldehyde quantitatively in a mouth-wash by the well-known methods, including the hydrogen peroxide, the iodine, and the ammonia methods, gave unsatisfactory results, probably owing to the presence of a

large number of different bodies, both organic and inorganic. A method found satisfactory was as follows:—Ten c.c. of the sample (containing about 0.2 per cent. of formaldehyde) are treated with 2 c.c. of concentrated hydrochloric acid and 10 c.c. of *N* silver nitrate solution, shaken, 4 c.c. of 30 per cent. sodium hydroxide solution immediately added, and the flask shaken again and left for 15 to 30 minutes, with occasional shaking. In the presence of formaldehyde the mixture immediately turns black. It is filtered, the precipitate washed with hot water, and the filter perforated by means of a thin stirring rod and rinsed with nitric acid (1:3) to dissolve all the reduced silver, leaving the excess of the silver chloride undissolved. After some dilution the silver chloride is filtered off, and the filtrate stirred with sufficient hydrochloric acid to precipitate the silver, which is determined in the usual manner, and converted into the corresponding amount of formaldehyde. $2\text{AgCl} = 1\text{CH}_2\text{O}$.

The following results were obtained:—

					Formaldehyde. Per Cent.
Iodine method	0.019
Hydrogen peroxide method	0.63
Silver chloride method	0.20
Actual content	0.20

The method is only applicable in the absence of sugars.

Should there be any doubt that the black precipitate is due to formaldehyde, various qualitative tests, such as the resorcinol test, may be applied to the distillate from the original preparation.

OSCAR HEIM.

244, EAST STREET 81, NEW YORK.

CORROSION-RESISTING STEEL FOR LABORATORY USE.

FOR some months past capsules of corrosion-resisting (stainless) steel have been used in this laboratory for the determination of total solids of milk and other foods.

Solutions containing fruit acids, vinegar or caustic soda of decinormal strength have no effect upon the steel, when evaporated to dryness therein on the water-bath.

A suitable size of flat-bottomed dish, somewhat similar to the porcelain milk capsule, has an outside diameter of 3 inches and is $\frac{3}{8}$ inch deep, with sloping sides and rounded corners. In gauge 24 and highly polished the weight is from 20 to 30 grms.

These dishes have the advantages over porcelain of durability and greater heat conductivity, leading to rapid drying of contents.

Their unvarying weight after continued use proves them superior to either aluminium or nickel.

The dishes at present in use have been made to the above specification in "E.R.A. C.R.1." Corrosion-resisting Steel by Messrs. Hadfields, Hecla Works, Sheffield, at my request.

G. A. STOKES.

ANALYTICAL LABORATORY,
179, EDGWARE ROAD, W.2.

Notes from the Reports of Public Analysts.

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF BIRMINGHAM.

REPORT OF THE CITY ANALYST FOR THE FIRST QUARTER, 1929.

DURING the quarter the total number of samples submitted under the Food and Drugs Act was 1275, of which 1193 were bought informally (53 adulterated) and 82 under the provisions of the Acts (20 adulterated).

BEEF SUET.—Six samples of beef suet, bought from butchers, contained 0·8 to 1·6 per cent. of moisture, 0·1 to 0·3 per cent. of ash, and up to 0·5 per cent. of fat-free membrane. All the samples contained 98 per cent. or more of fat.

Eleven samples of *shredded beef suet* contained from 0·7 to 3·5 per cent. of moisture, and from 9 to 16 per cent. of rice or wheat flour, while the fat present varied from 82 to 90 per cent. In each case the samples were marked that they were sold as mixtures, and each contained less fat than butcher's beef suet.

Five of them, however, claimed that the article was so rich in fat that 1½ lbs. equalled 2 lbs. of raw suet, and one directed that one-third less than raw suet should be used. These labels are false, as, owing to the addition of flour, beef suet contains more fat than shredded suet. In two cases similar comparisons were made with lard, and as lard is practically pure fat, this statement made the absurd claim that their article equalled 133 per cent. of fat. In each case the vendors were cautioned, and the manufacturers undertook to alter their labels.

ALLEGED LOSS OF MOISTURE IN SUGAR.—In connection with prosecutions by the Weights and Measures Department for deficiency of weight in granulated sugar that had been weighed ready for sale, the amount of moisture was determined in eight samples. Three of them lost no moisture on heating and the other 5 lost 0·01 to 0·03 per cent., disproving the suggestion of the defendant that granulated sugar was liable to lose moisture after being weighed up for sale.

PRESERVED SAUSAGE.—The three samples analysed were incorrect, as they did not contain any preservative. Vendors should make a distinction between sausage and preserved sausage.

IODINE SOLUTION.—The 1885 British Pharmacopoeia ordered a "solution of iodine" which contained 5 per cent. each of iodine and potassium iodide dissolved in water, but the article has not been contained in subsequent Pharmacopoeias. The British Pharmaceutical Codex has a "Diluted Solution of Iodine" which contains 5 per cent. of iodine and 7·5 per cent. of potassium iodide dissolved in water, and a Canadian formulary has a similar preparation.

The single informal sample examined was labelled, "Iodine Solution. Poison. Paint on the affected part with a camel hair brush." It contained only 0·8 per cent. of iodine dissolved in iso-propyl alcohol and not potassium iodide; it did not comply with any of the above standards. It barely coloured the skin when used as a paint and was probably useless. The vendor was cautioned.

SYRUP OF SQUILL.—This drug should contain at least 67 per cent. of sugar, which may become more or less changed into invert sugar. One informal sample contained only 51 per cent., and the vendor was cautioned. The other seven samples were genuine.

J. F. LIVERSEEGE.

METROPOLITAN BOROUGH OF STEPNEY.

ANNUAL REPORT OF THE BOROUGH ANALYST FOR 1928.

THE 1528 samples taken under the Food and Drugs Acts comprised 968 formal samples and 560 informal samples; 68 samples were adulterated.

GROUND GINGER.—Six of 11 samples examined were found to be adulterated with sulphur dioxide in amounts ranging from 30 to 1260 parts per million. The vendors were cautioned. Ginger may contain preservative if it is to be used in the preparation of one of the goods in which preservative is allowed (*e.g.* ginger wine), but if bought for the purpose of making cakes or puddings, it may not contain sulphur dioxide.

AMMONIATED TINCTURE OF QUININE.—A sample was found to be 15·8 per cent. deficient in ammonia. The vendor stated that he had had one pint of the tincture in stock for three days only, and that it must have been received by him at practically the same strength as that at which he had sold it. The wholesale druggists concerned made themselves responsible for the defence. The loss was attributed to evaporation of the ammonia during manufacture and while opening the bottle during dispensing, but rebutting evidence was given by the prosecution, and finally the vendor was fined £2 with £15 15s. costs (*cf.* ANALYST, 1929, 418).

CARBON DEPOSIT FROM ETHYL PETROL.—A sample obtained from the cylinder of a motor vehicle which had been running on ethyl petrol was found to contain 17·1 per cent. of lead, or 23·1 per cent. on the oil-free substance. From the total sample 2·86 grms. of metallic lead, mostly in a very finely divided state, were obtained.

DOUGLAS HENVILLE.

Legal Notes.

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

MILK CHEESE.

ON June 19 a grocer was summoned at Salford for selling cheese not of the quality demanded, and a dairy company was summoned for issuing a label which falsely described the article.

The certificate of the Public Analyst (Mr. H. H. Bagnall) stated that the cheese contained: Fat, 2·0; protein, 17·5; water, 72·5; mineral matter, 4·5; lactic acid, lactose, etc., 3·5. The following comment was made: "A genuine milk cheese should contain at least 45 per cent. of fat, calculated on a water-free cheese, whereas this sample contains 7·3 per cent. calculated in this way, and is therefore deficient of 83·3 per cent. of the minimum amount of fat."

On the label of the wrapper were the words: "The Bondon Milk Cheese. Delicious. Made by . . . Dairies."

The Inspector said that the price paid for the cheese was equivalent to 1s. 2d. per lb. In reply to the solicitor for the defence, the witness agreed that there was no standard with regard to cheese under the Food and Drugs Act, but said that there was a custom. A milk cheese should be made from milk, not from separated milk. This cheese had only about a third of the value of ordinary cheese; Cheshire cheese made from whole milk could be bought at 10d. per lb.

For the defence it was stated that the cheese was made from separated milk, with the addition of a little whole milk, and the contents were absolutely pure. The manufacturers had used the words "Milk Cheese," with the idea of avoiding any confusion with what was known as cream cheese. The wording of the label had now been altered.

The Stipendiary said that the company must take the responsibility for the shopkeeper, who would be discharged under the Probation of Offenders Act, and the company would be fined 10s. 6d. with £5 5s. costs.

ADULTERATED PEPPER. INTERMEDIATE WARRANTY.

On June 19 a provision dealer was summoned at Tower Bridge Court for selling pepper adulterated with 50 per cent. of ground rice, and a firm of wholesale grocers was summoned for giving a false warranty.

Mr. P. Robinson, for the Bermondsey Borough Council, said that the warranty given to the retailer was not disputed, and the Council would not object to the case against him being dismissed on that ground. The Magistrate (Mr. Tassell) agreed, and the summons against the first defendant was dismissed.

There were two summonses against the wholesale firm, one under Sec. 29, for selling to the prejudice of the purchaser, and the other, under Sec. 30, for giving a false warranty. On the first summons the seller was entitled to serve notice of a warranty.

Sir R. Aske, appearing for a firm of importers, said that notice of a warranty had been served on them for selling the pepper to the wholesalers.

Mr. Robinson, continuing, said that the defendant could be discharged, provided that he proved to the satisfaction of the Court that, having bought the pepper under a warranty, he sold it as he received it, and that he had no reason at the time to believe it was otherwise than pure. If a person sold under a warranty, and that warranty proved to be false, then the onus of proof was cast upon the giver of that warranty, and the warrantor in this case had to prove that he did not rely upon the warranty received until he had taken steps to satisfy himself that it applied to the goods received.

An inspector had sampled a keg of the pepper as it was being delivered to the retailer, and had found it to be adulterated in the same way as the original sample. It was not suggested that the defendants had adulterated the pepper, but the case for the local authorities was that this firm (who had a number of local shops), when acting as wholesalers, should have convinced themselves that the article they had supplied complied with the description they had given of it.

Mr. Frampton, for the defence, said that he would prove the warranty and confine himself to the second summons, for giving a false warranty. The firm, which had been established since 1668, had placed orders for various articles with the firm of importers, and since January of this year had purchased exclusively from them their bulk of pepper, about 3 tons, of three kinds, one known as S.A.C., for which they paid 2s. 4d. per lb. They had received no complaints from anyone about the goods they had bought from this firm until the present one. They then suspended the sales of all peppers, wholesale and retail, and called in Dr. Dyer to analyse all the peppers they had in stock. His analyses showed that the only adulterated pepper was the brand "S.A.C."

On every order the defendants printed the words: "Goods included in this order are to be guaranteed of the nature, substance and quality demanded." On each invoice sent by the importers was printed: "All the goods on this invoice are

warranted to be of the nature, substance and quality demanded under the Food and Drugs Act now in force, and are sold as such." He submitted that when a person bought goods under a warranty and sold them under a warranty, he was entitled to carry over to the purchaser the warranty he had received, and that he was protected as much as his own customer. In a similar case which went to the High Court (*Bell and the Dairy Supply Co. v. Houghton*) in 1911, it was held that where goods were bought under a warranty and sold to a customer under a warranty, that warranty held. He submitted that if he established his warranty, that was an answer to the summons for giving a false warranty.

The secretary of the defendant firm gave confirmatory evidence. He had no reason to suspect the genuineness of the pepper supplied or the truth of the warranty. In cross-examination, he admitted that they had had no analysis made until after the complaint. If they had everything analysed which they bought under a warranty, they would require an army of analysts.

The Magistrate observed that the firm seemed to have taken every reasonable, commonsense precaution from the business point of view. Under Sec. 30 a defendant was entitled to say that he had every reason to believe the description he had received under a warranty to be true, and when a reputable firm with a record like that of the defendants took every precaution, he could not believe that there was anything more to be done. Both summonses would be dismissed on the warranty.

ARTIFICIAL CREAM.

On August 13 a "Pure Milk and Cream Company, Ltd.," was summoned at Marlborough Street Police Court for selling a substance purporting to be cream or artificial cream without having the word "cream" immediately preceded by the word "artificial" on the label, as required by the Artificial Cream Act, 1929; also for using a receptacle for the conveyance of cream without having the words "artificial cream" on it.

Mr. G. B. McClure, who appeared for the prosecutors, the National Farmers' Union, said that the Artificial Cream Act, 1929, was passed in order that a purchaser might know that he was getting artificial cream, which, in this case, could not be distinguished by analysis from ordinary cream.

Mr. B. M. Cloutman, for the defence, submitted that the National Farmers' Union was not entitled to prosecute, and that proceedings could only be taken by authorities administering the Food and Drugs Acts. The Farmers' Union had laid the information as common informers.

The Magistrate (Mr. Mead) said that the term "common informer" referred to a person who was to receive a share of the plunder. A person acting in the public interest and receiving nothing for it was in a different category.

Mr. Cloutman contended that there had only been a technical infringement of the Act. The prosecution had been brought only six weeks after the Act had been passed, while things were in a transition stage, and the fact that the food and drug authority had not seen fit to take action was a complete answer to the charge.

Mr. Mead ruled that the summons was in order. According to the Act: "It shall be the duty of every food and drug authority to enforce the provisions of this Act," but that did not prevent other people prosecuting if the food and drug authority was not sufficiently vigilant.

After evidence of the purchase and of the fact that there was no mention of artificial cream on the carton had been given, the company's sales manager gave evidence that a supply of labels and cartons complying with the Act had been

ordered immediately after the Act had been published, but that for a few days it had been necessary to use the old cartons.

In cross-examination the witness, whose attention had been called to the words on the cartons, "Specially authorised by Act of Parliament," said that he considered that the Act was passed for their benefit.

Mr. Mead, giving judgment, said that he considered the name of the company to be misleading, since an ordinary person would think that it referred to natural milk and cream. He supposed that the Act had been passed to protect the interests of farmers in this country. It might be that manufactured cream contained fewer malignant germs than natural cream, but, whether that was so or not, there was a prejudice in favour of natural cream. The price of natural cream was higher than that of the manufactured article, and therefore he thought that farmers had a right to be protected, as they were protected by the Act. Nobody could complain that, as soon as the Act was passed, the persons interested took care to see that it did not become a dead letter.

In his opinion the label was absolutely misleading. There was nothing about the cream being artificial until the label was turned round, and then the words were upside down. The label on the top had the same fault, and there was nothing on the front to show what the article was. The fact that the cream was artificial ought to be made more conspicuous. The artificiality of the cream ought not to be concealed, but should be made more prominent than anything else. In the event of another prosecution, and if this label were produced, he would probably hold that it did not comply with the Act. It was an evasion of the Act, since the public could only see that the cream was artificial by scrutinising the carton. He did not regard the offence as a technical one.

A fine of £10 2s. with £7 costs was imposed.

Mr. Cloutman asked the Magistrate to state a case on the preliminary point that he had raised, and to this Mr. Mead agreed.

"CHLORODYNE B.P. '85" WITHOUT MORPHINE.

ON July 25 a firm of drug store keepers was summoned at East Ham Police Court for having sold a bottle of liquid falsely described as "Chlorodyne B.P. '85," contrary to the Merchandise Marks Act, 1887.

Mr. H. Glyn-Jones said that the Pharmaceutical Society, in accordance with its duties, had purchased, through an inspector, a bottle of liquid labelled "Chlorodyne B.P. '85." Originally the name "Chlorodyne" was that of a proprietary medicine introduced into this country about the middle of the last century, and it then contained chloroform, morphine, and dilute prussic acid. The name had since been extended to a number of similar preparations, not necessarily having the same formula, but in the British Pharmacopoeia of 1885 a specific formula was given, containing both morphine and dilute prussic acid. The defendants were in a dilemma. If they sold chlorodyne containing poison, they were committing an offence for which the Society could recover penalties. If they omitted the morphine they were committing an offence under the Merchandise Marks Act. There was an obvious danger that if the public bought an article labelled "Chlorodyne B.P. '85," they might suffer serious consequences, owing to the presence of morphine in one preparation but not in the other.

Mr. Duthie, for the defence, said that his clients had no alternative but to plead guilty. If the allegation had been that they had been selling this preparation simply as "Chlorodyne," it might have been another matter. The defendants had

actually been selling it for some time without the words "B.P. '85" on the label, but when renewing their labels they had not noticed that the new stock bore the words "Chlorodyne B.P. '85." As there was no morphine in the preparation, he asked that as lenient a view as possible might be taken.

The Stipendiary (Mr. W. W. Paine) observed that it seemed to him that, as one of the most important ingredients in the correct composition of chlorodyne was morphine, as a sedative, selling it without that was, in his opinion, a distinct fraud. He inflicted a penalty of £20, with £5 13s. 0d. for Court and special costs,

Ceylon.

REPORT OF THE GOVERNMENT ANALYST FOR 1928.

IN his annual report the Government Analyst (Mr. C. T. Symons) states that 1046 reports were made, and that 3881 articles were examined, this being a large increase on the preceding year.

MILK.—Of the 321 samples examined, only 27 were genuine; 170 of the samples contained over 25 per cent. of added water, 38 contained more than 60 per cent., and 12 contained more than 70 per cent., the maximum adulteration figure being 77 per cent. It is hoped that this appalling state of affairs does not represent a fair picture of the out-station milk supplies of the Island. There is much agitation to obtain purer water supplies, and, incidentally, this would ensure a less dangerous milk supply.

CRIMINAL INVESTIGATION WORK.—During the year there were 362 cases involving the examination of 904 exhibits. There were 78 poisoning cases (with 199 exhibits), and in 20 cases (with 39 exhibits) poison was detected. The poisons found included prussic acid (3 cases), arsenic, strychnine, acetic acid and mydriatic alkaloids (2 each), mercury, copper sulphate, croton seeds, datura seeds, hydrochloric acid, *Cerbera odollam*, kerosine oil, poisonous fish, and an unidentified poison (1 each).

Powdered glass was found in one instance, though it is doubtful whether this is to be considered an active poison if the literature on the subject is to be trusted. In this case, however, the powder also contained two teeth from a venomous snake, and some unidentified toxic substance. The intended victim noticed that the rice with which the powder was mixed had a peculiar colour, and on enquiry, was told that this was due to the rice having been boiled in a pot in which tea had been made. As the rice tasted gritty, he threw it out and washed his mouth.

Poisonous Fish.—The case of poisoning from eating some cooked fish in the Matara District is of interest. The symptoms shown by the victims were vomiting, diarrhoea and giddiness, and ended in death in a short time. The fish was apparently *Clupea moluccensis*, which is found off the Southern Coast, and is poisonous at certain seasons of the year. Some years ago there was a similar case.

***Cerbera odollam*.**—The seeds of this plant, known locally as *veta kaduru*, contain toxic constituents. The case reported was one of suicide.

CASES OF FRAUD.—One interesting case necessitated the laborious reconstruction of a counterfeit Rs. 50 currency note from pulp chewed in a man's mouth. Apparently when this person was arrested, he at once put the note into his mouth

and chewed it up. It was forcibly removed from his mouth in a pulpy and fragmentary condition. The time spent on the work of teasing out the pulp and piecing the note together were well rewarded by the discovery that it was the work of a particular forger, whose work had appeared in the laboratory on a previous occasion.

The most interesting investigation was concerned with the alleged disappearance of most of the contents of a parcel of diamonds sent to Ceylon by registered post. The parcel, when received from the postal authorities, appeared to have all its seals intact. When opened it was evident that most of the contents had been abstracted through a hole in the tin container. Examination of the paper wrapping showed that one of the seals had been carefully cut out, leaving the tin exposed. A round hole was then made in the tin and the diamonds abstracted. Then melted sealing wax was poured on the hole and the original seal was replaced. The edges were slightly heated to make the wax of the original seal unite with the wax put on later. The whole process was most ingeniously carried out, but careful microscopical examination by ultra-violet light showed quite clearly the manner in which the fraud was carried out. Subsequent confession on the part of the culprit has shown that he did actually use the method indicated by the original examination of the packet.

THE MERCURY VAPOUR LAMP.—Some of the uses to which this lamp has been put are the following:—

(1) A seminal stain on a fabric can be localised as soon as it is seen under the lamp, and can then be removed for complete identification. This is much more rapid and certain than the old method of relying upon tactile sensation.

(2) Bleached ink writing appears clearly with almost its original darkness. This has been used many times to detect the use of stamps which have been used a second time. Such stamps, originally attached to deeds or share transfers, bore ink writing as initials and dates. This ink writing has been chemically bleached, leaving in certain cases a very passable presentation of a new unused stamp, when the process has been skilfully carried out. If one may judge by the large numbers which have been examined in these laboratories such cleaned stamps have a ready market, and many have appeared on notarial deeds, being accepted as unused stamps. Under ultra-violet light, the fraud is at once visible. In one case, which is certainly the first case in Ceylon, and possibly the first case in the East, the lamp was used in court, being connected with the electric light circuit in the Police Court, and the Police Magistrate was able to see the original writing on the stamps, which under ordinary light was quite invisible.

(3) In a case of a motor car accident from Nuwara Eliya a large number of small fragments of glass, picked up on the road and in a garage, were sent for examination to determine whether any of them, and, if so, which, corresponded with certain broken portions of the headlight lens of the car concerned. Owing to the fact that the lens glass had a peculiar fluorescence under the ultra-violet light, it was possible to pick out the corresponding pieces at once, without going to the trouble of making what would have been a very long and troublesome analysis of the glass.

(4) It was reported that certain artificial manure on a paddy field had been stolen from a particular stock. Specimens were examined under the ultra-violet lamp, and it was found that there was no resemblance between the two.

(5) The lamp has been found of great use also in the examination of counterfeit currency notes.

THE FÉRY SPECTROSCOPE.—This has been introduced for the rapid qualitative analysis of metals, and especially for tracing small impurities. By this means a photograph may be taken of the ultra-violet end of the spark spectrum of the specimen, and a comparison made with standards, or with another sample reported to be from the same source. The instrument used is only a small one, the larger pattern being very costly, and has only been in use a short time. But it is hoped that it will be of great utility in comparing, for instance, lead slugs used in shooting cases with lead found on the accused's premises, and in determining the composition of counterfeit coins without using more than a very small piece of the coin.

CHINESE CRACKERS.—No less than 69 batches of these were examined to determine whether they complied with the Customs regulations as regards import, and many were found which contained a chlorate in place of the nitrate which is alone permissible. It must be remembered that several years ago Chinese crackers were exempted from the ordinary regulations covering the import of explosives and fireworks, and could be sold without licence, since, as imported at that time, they were loaded with black powder, had little explosive power, and were thus considered to be comparatively harmless. During recent years very much larger crackers have been imported with a charge of high explosive power, consisting of aluminium powder with an oxygen carrier. These were obviously dangerous and were prohibited, but after this the manufacturers, presumably in order to provide a cracker with more explosive power than the old black powder one, used potassium chlorate in place of the nitrate, and again contravened the regulations.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Evaluation of Crab Preparations and Detection of Crab Ingredients.

G. Büttner and A. Miermeister. (*Z. Unters. Lebensm.*, 1929, 57, 431–437.)—Genuine crab preparations contain three natural colouring matters—the green or blue “cyanocrystallin,” the red “crustaceorubin,” and the yellow “crustaceofulvin,” all of which are lipochromes and are soluble in oils and in organic solvents, but not in hot or cold water, acids or alkalis. Cooking transforms the first into the second-named colour, so that red predominates. Concentrated sulphuric acid or alkaline potassium iodide solution produces a blue-green colour, but no characteristic luminescence is produced in ultra-violet light, though the uncoloured portion (flesh and muscle) of the crab gives a pale blue light. Dyes used to imitate crab colour (Orange I, II, G and GG, Tropaeolin and Tropaeolin 000) are usually soluble in water, fat, and alcohol, and may be detected by the fact that they are rapidly destroyed by reduction with zinc and hydrochloric acid, but not with nitrites or sulphites, whilst the natural colour is stable. For the test 20 grms. of sample are ground in a mortar with sand, and heated under a reflux condenser with 150 c.c. of 96 per cent. alcohol for 3 hours. The fat is separated from the filtered liquid by cooling it in ice-water for 2 hours, the liquid re-filtered, evaporated

to 10 c.c., cooled and again filtered. The filtrate is shaken with 2 c.c. of zinc chloride solution and 2 c.c. of hydrochloric acid; if the solution is colourless after 1 hour, no natural colour is present. Yellow to red colours indicate increasingly large proportions of natural colour. Wool tests will not distinguish natural and artificial colours. Ultra-violet light destroys the genuine colour completely, and daylight destroys it partly, but the colour is stable in the dark. A 0.1 *N* solution of sodium dichromate was used as colour standard for these tests.

J. G.

Normal Occurrence of Arsenic in Fish and in Cod-liver Oil. E. Sadolin. (*Dansk. Tids. Farm.*, 1928, 2 (7), 186; *Chem. Abs.*, 1929, 23, 210.)—Two samples of codfish flesh gave, respectively, 0.4 and 0.8 mgrm. of arsenic per kilo; cod-liver, 0.7 and 3.2 mgrm.; and for cod-liver oil, 3.0 to 4.5 mgrm. was the normal figure. Eel oil, extracted by ether, contained 0.6 mgrm. of arsenic per kilo., herrings (muscular tissue) 2 mgrms. per kilo., and (oil) 9 mgrms., per kilo.

D. G. H.

Seed Fats of some Cultivated Species of Umbelliferae. B. C. Christian and T. P. Hilditch. (*Biochem. J.*, 23, 327–338.)—The percentage compositions of the fatty acids obtained from certain fats were:

			Palmitic acid.	Petroselinic acid.	Oleic acid.	Linolic acid.
Fennel	4	60	22	14
Carrot	4	58	14	24
Coriander	8	53	32	7
Celery	3	51	26	20
Parsnip	1	46	32	21
Chervil	5	41	0.5	53.5
Caraway	3	26	40	31

The view that petroselinic acid ($\Delta^6:7$ -octadecenoic acid) is characteristic of umbellate seed fats is strengthened. In all cases considerable amounts of resinous and unsaponifiable matters were present; this makes the quantitative results somewhat less certain than in their absence. An attempt to determine whether the composition of the endosperm fat differed from that of the fatty oil was inconclusive.

D. G. H.

Quantitative Examination of the Kreis Rancidity Reaction. J. Pritzker and R. Jungkunz. (*Z. Unters. Lebensm.*, 1929, 57, 419–421.)—One drop (0.5 mgrm.) of a fresh aqueous 1 per cent. solution of acrolein are mixed with 3 drops of 3 per cent. hydrogen peroxide solution in a stoppered cylinder, and after 3 hours in darkness 5 c.c. of concentrated hydrochloric acid (sp. gr. 1.19) are added, and the mixture shaken for 1 minute. After the addition of 5 c.c. of a 1 per cent. solution of phloroglucinol in ether a bright red colour is obtained which reaches a maximum after 5 minutes, and, if produced from 0.5 mgrm. of acrolein, may be matched in shade by 1.2 mgrms. of potassium permanganate in 100 c.c. of water (or 3.8 c.c. of 0.01 *N* solution). In this version of the Kreis test the acrolein is completely oxidised by the hydrogen peroxide to epihydrinaldehyde,

the sensitiveness of the test being 1:100,000, and the upper detectable limit 10 mgrms. of aldehyde in 100 c.c. of oil. The method has been compared with that of von Fellenberg (ANALYST, 1925, 50, 245), and 10-year old samples of olive, soya and maize oils, arachis oil (2 years), lard (1 year) and butter fat (14 years) were found to contain 60, 60, 20, 100, 200, and 400 mgrms. of epihydrinaldehyde per 100 grms., respectively. Since, in the extreme case, the proportion of decomposed fat corresponds with about 13 times the amount of aldehyde found, these samples were decomposed to the extent of 0.3 to 5 per cent. (cf. ANALYST, 1926, 51, 635; 1929, 411). J. G.

Detection of Rancidity in Fats from intact Seeds and Fruits. A. Niethammer. (*Z. Unters. Lebensm.*, 1929, 57, 358-360.)—The sample is well disintegrated in a dish, placed in a linen bag previously extracted in succession with acetone and chloroform and washed with distilled water, and extracted with petroleum spirit under a reflux condenser. The solvent is distilled from the extract, and the Kreis and Fellenberg tests applied (Pritzker and Jungkunz, ANALYST, 1926, 51, 635). Old samples of *Zea mays*, *Linum usitatissimum*, *Cannabis sativa*, *Helianthus annuus*, and *Papaver somniferum* gave positive results, but fresh samples gave no reaction. J. G.

Fatty Acids Associated with Rice Starch. L. Lehrman. (*J. Amer. Chem. Soc.*, 1929, 51, 2185-2188.)—An investigation of the fatty acids associated with rice starch (α -amylose portion) disclosed the presence of 36 per cent. of palmitic acid, 35 per cent. of oleic, and 29 per cent. of linolic acid. There were probably no other substances in the fatty acid mixture obtained by extracting the solid material resulting from the hydrolysis of rice starch. D. G. H.

Petroleum Spirit Test for Purity of Castor Oil. T. Cocking. (*Pharm. J.*, 1929, 123, 11.)—The limits of the Pharmacopoeia petroleum spirit solubility test are considered too wide to justify its retention. Pure castor oil was found not to pass the test unless some aromatic hydrocarbon was present in the spirit. With pure hexane as solvent the clearing points showed a divergence of as much as 9.5° for different genuine oils, and a clearing point of 22.3° C. given by one genuine oil corresponded with that given by another genuine oil to which 9 per cent. of olive oil had been added. D. G. H.

New Reaction for the Identification of Urotropine in Wines. M. V. Ionescu and C. Bodea. (*Bull. Soc. Chim.*, 1929, 45, 466-468.)—The following reaction serves for the detection of urotropine or formaldehyde in sulphited or non-sulphited wines. The clear wine (2 to 5 c.c.) is treated with 1 to 2 volumes of 0.7 per cent. aqueous dimethyl-dihydro-resorcinol solution. The separation of a white crystalline precipitate of methylene-bisdimethyl-dihydroresorcinol, with m.pt. 184-187°C., after about 15 minutes, or sooner if the liquid is boiled, indicates either formaldehyde or urotropine. The reaction is given by 0.02 grm. of urotropine, or the corresponding amount of formaldehyde, per litre of wine. T. H. P.

Chemical Constitution of the Gums. Part I. Nature of Gum Arabic and the Biochemical Classification of the Gums. A. G. Norman. (*Biochem. J.*, 1929, 23, 524-535.)—A detailed examination of acid gum arabic showed the acid group to be of the uronic type, and the only two sugars present to be galactose and arabinose. The acid hydrolysis products were obtained by boiling the gum with 3 per cent. sulphuric acid for a definite period, and, while still very hot, neutralising the acid by finely divided barium carbonate, and, after a few moments, filtering off the precipitate. Boiling alcohol is poured into the hot filtrate until the alcohol concentration reaches 60 per cent., when the precipitate settles quickly, and the supernatant liquid is at once poured off. The end product is thus free from galactose and arabinose. The precipitate is dissolved in water, the solution filtered, heated nearly to boiling, and reprecipitated, and this process is repeated several times. Analyses of the original product after 1, 3 and 5 hours' hydrolysis were made, and it is concluded that gum arabic has no definite empirical formula, but probably consists of a nucleus acid made up of galactose and a uronic acid, probably galacturonic acid, to which is linked arabinose by glucosidic linkages, so that the arabinose is more easily split off than the other components. The structural resemblance to hemicellulose is close, and it is suggested that protracted mild oxidation of linked hexose, and particularly galactose units, results in the formation of pectin, hemicelluloses and gums. The analysis of one sample of acid gum arabic gave the following results:—Ash, 0.24; furfuraldehyde yield (ash-free), 13.93; carbon dioxide yield (ash-free), 4.39; uronic acid anhydride, 17.56; furfuraldehyde due to uronic acid, 2.91; anhydroarabinose, 20.52; and anhydrogalactose (yielding arabinose 23.52, and galactose 68.80 per cent.), 61.92 per cent.

D. G. H.

Determination of Pyrethrin I and II in Pyrethrum. F. Tattersfield and R. P. Hobson. (*J. Agric. Sci.*, 1929, 19, 433-437.)—As the acid method of determining pyrethrin I and II (*ANALYST*, 1929, 351) requires several days for its completion, the following rapid method has been devised for the evaluation of pyrethrum by determining pyrethrin I, which is the more important of the two poisons present. Ten grms. of the ground pyrethrum are extracted in a Soxhlet apparatus with petroleum spirit (b.pt. 40° to 50° C.), which is kept vigorously boiling over a carbon-filament lamp. When the solvent draining over is colourless, the petroleum spirit solution, which should have a volume of about 50 c.c., is placed in a long-necked 100 c.c. flask to be used for the subsequent distillation, the extraction flask being rinsed once with a little petroleum spirit. After addition of 4 to 5 c.c. of *N*-sodium hydroxide (in methyl alcohol), the mixture is boiled under a reflux condenser on a water-bath for 1½-2 hours. The liquid is acidified with *N*-sulphuric acid and steam-distilled. When 50 c.c. of aqueous distillate have collected below the petroleum spirit the receiver is changed, and a further 50 c.c. are collected. The first distillate is vigorously shaken for a minute in a fairly large separating funnel, the aqueous layer being separated and the petroleum layer washed once with water and run into a flask containing 20 c.c. of water, a few

drops of alcohol, phenolphthalein, and just enough alkali to give a faint pink colour. Titration with *N*/50 soda is carried on until the aqueous layer is distinctly alkaline after vigorous shaking in the corked flask. The second 50 c.c. of distillate are added to the first aqueous fraction (already extracted once), and the whole vigorously shaken with 50 c.c. of petroleum spirit, the washed petroleum layer being added to the titration flask, and the titration finished as before; very little additional alkali is usually needed. After deduction from the titration reading of a blank determined for the petroleum spirit (about 0.2 c.c. of *N*/50 soda), the monocarboxylic acid and pyrethrin I contents may be calculated: 1 c.c. *N*/50 alkali = 3.36 mgrms. monocarboxylic acid = 6.6 mgrms. pyrethrin I.

T. H. P.

Determination of Ammonia and Amide Nitrogen in Tobacco by the Use of Permutit. H. B. Vickery and G. W. Pucher. (*J. Biol. Chem.*, 1929, **83**, 1-10.)—The accurate determination of the pre-existing ammonia or of the amide nitrogen of tobacco is rendered difficult by the volatility of nicotine which distills over more or less completely when the standard procedures for the determination of these forms of nitrogen are used; no satisfactory correction method for the nicotine content of such distillates has yet been found. During an investigation of the tobacco leaf it became necessary to determine accurately the simpler forms of nitrogen in the green leaf as well as in manufactured tobacco, and a method which was devised for the determination of pre-formed ammonia and of amide nitrogen in the tobacco is now described. The ammonia is distilled from the untreated or hydrolysed sample into acid, according to the technique of Folin and Wright (*J. Biol. Chem.*, 1919, **38**, 461), then, as described by Folin and Bell (*J. Biol. Chem.*, 1917, **29**, 329), removed by permutit, liberated subsequently from the permutit by alkali, and determined colorimetrically by the use of Nessler's reagent. The nicotine does not interfere; it is absorbed by permutit only to a very small extent, and gives no appreciable colour with Nessler's reagent. The base exchange relationships of monomethyl-, dimethyl- and trimethylamine with permutit were also studied; none of these amines interferes with the determination of ammonia, although data by Whitehorn (*J. Biol. Chem.*, 1923, **56**, 751; *ANALYST*, 1923, **48**, 565) indicated that nicotine and several of the volatile amines undergo extensive base exchange with permutit. The new method is simple and rapid and can readily be employed in the investigation of other tissues. Ammonia added to tobacco extracts can be recovered with an average accuracy of 95 per cent. Amide nitrogen of asparagine added can be recovered with an average accuracy of 92.5 per cent.; this lower result is to be expected, as the proportion of amide nitrogen is calculated from the difference in ammonia content before and after hydrolysis, and therefore contains the error of the ammonia determination twice over.

P. H. P.

Caffeine-Salicylic Acid a Molecular Compound. N. Schoorl. (*Pharm. Weekblad*, 1929, **66**, 357-358.)—The solubility of caffeine in water (2 per cent.) is increased if the caffeine is combined with salicylic acid (*ANALYST*, 1924, **49**, 486), and the air-dried commercial sodium salt, $C_8H_{10}N_4O_2$, $C_7H_5O_3Na$, $5H_2O$, prepared

by crystallisation from warm water of an equimolecular mixture of sodium salicylate and caffeine ($C_8H_{10}N_4O_2$, $5/6H_2O$) contains 20.2 per cent. of water of crystallisation. It is pointed out that the whole of the water of crystallisation is removed after 1 day in a desiccator, and the requirements of the Dutch Pharmacopoeias are criticised from this point of view.

J. G.

Salicyl-sulphonic Acid. J. Rae. (*Pharm. J.*, 1929, 122, 618.)—Seven samples of salicyl-sulphonic acid were examined for colour and moisture percentage, purity (by titration with 0.1 *N* sodium hydroxide), sulphate (by the U.S.P. turbidity method), free salicylic acid, and m.pt. The results showed that two salts are on the market, one with a m.pt. of about 110° C. and the other of 120–124° C. The other results, although varying somewhat, did not fall into coinciding groups.

D. G. H.

Quantitative Determination of Methylene Blue. M. François and L. Sequin. (*J. Pharm. Chim.*, 1929, (8), 10, 5–9.)—Owing to the increasing use of methylene blue in therapeutics the authors have devised a method for its quantitative determination. The principle of the method is based on the fact that methylene blue, which behaves analytically like an alkaloid, is completely precipitated by a solution of picric acid. A volumetric method was first tried, but, as titration with picric acid did not give a definite end-point, this was rejected in favour of a gravimetric method, the technique of which is as follows:—One grm. of methylene blue is weighed out carefully, and placed in a small conical flask. In order to obtain complete solution water is added in portions of 10 c.c., each portion is poured through a funnel, containing a small plug of cotton, into a 100 c.c. flask, the flask and funnel are washed, the contents made up to 100 c.c., and the flask shaken. Ten c.c. of this solution (which contain 0.1 grm. of methylene blue) are placed in a 125 c.c. conical flask, and 20 c.c. of an aqueous solution (5 grms. per litre) of picric acid are added. Immediately a purple-black precipitate is formed and leaves a clear yellow solution. After filtration the precipitate is carefully washed with 10 c.c. of water to remove any excess of picric acid, pressed lightly between filter papers, then left to dry (either in the air or in a desiccator over sulphuric acid), and weighed. The crystalline picrate which is precipitated is formed of one molecule of methylene blue and one molecule of picric acid with no water of crystallisation. The molecular weight of picric acid is 229, that of methylene blue 373.5 (with 3 molecules of water), or 319.5 (anhydrous); thus the molecular weight of the picrate is 548.5. Therefore to obtain the weight of methylene blue, the weight of the dry precipitate is multiplied by $\frac{373.5}{548.5}$, or 0.6809.

Analyses of pure samples which have been carried out show very satisfactory results with this method. When solutions have to be analysed, amounts which contain approximately 0.1 grm. of methylene blue should be taken. If other compounds are likely to be present, care must be taken to eliminate first of all the substances which may be precipitated by picric acid, such as alkaloids, albuminoids and ammonium and potassium salts.

P. H. P.

Detection of Isopropyl Alcohol in Cosmetics by Means of Piperonal.

G. Reif. (*Z. Unters. Lebensm.*, 1929, 57, 277-288.)—The author's method (*ANALYST*, 1928, 53, 497) is modified as follows:—The alcohol is removed from 10 c.c. of the sample by distillation on the water-bath, and collected in a receiver cooled in ice-water. To 1 c.c. of the distillate are added 3 c.c. of hydroxylamine hydrochloride solution containing 0.05 gm. for mouth-washes or scents and 0.1 gm. for hair-washes (which may contain tincture of cantharides). The mixture is well shaken, allowed to stand for 3 minutes at room temperature, 0.4 gm. of medicinal carbon (*Carbo medicinalis*) added, and the whole well shaken. After filtration through a dry paper into a 100 c.c. boiling flask, the clear liquid is mixed with 5 c.c. of a 0.5 per cent. solution of piperonal in absolute alcohol, and 20 c.c. of concentrated sulphuric acid (sp. gr. 1.84) added carefully, to avoid boiling. Five c.c. of the mixture are then heated on the water-bath for 5 minutes. In the absence of isopropyl alcohol a brown or green-brown colour appears, or in its presence a red or red-brown colour. If 30 c.c. of a 30 per cent. solution of acetic acid are at once added a greyish-yellow or transitory red colour is obtained in the absence of the alcohol, or a red-brown colour, turning red after 10 minutes, appears in its presence. The method was tested for a number of cosmetics of known and varied compositions, and shown to be independent of the presence of fusel oil, denaturants or other constituents. J. G.

Tin-Foil as a Packing for Rindless Cheese. Elten. (*Chem. Ztg.*, 1929,

53, 586.)—The foils examined contained 96 to 98 per cent. of tin, 2 to 4 per cent. of antimony, 0.1 to 0.2 per cent. of lead and traces of copper and iron, and were discoloured in places. The portions of the cheese in contact with the darkened portions contained 2.1 to 2.3 per cent. of tin, and had an acid of 2.4 to 2.6, whilst the acidity of the remainder was 1.6. The importance of the use of a good valve-quality product of low acid content, particularly when the melted cheese is allowed to set in its tinfoil container, is emphasised. J. G.

Lead in Red Glaze. A. Gronover and E. Wöhllich. (*Z. Unters.*

Lebensm., 1929, 57, 360-363.)—The red glaze or enamel of certain culinary ware may contain lead chromate, and the conditions of extraction of the lead for the purposes of analysis are discussed. It is recommended that the glaze be well scalded with hot water, two-thirds filled with 4 per cent. vinegar, and heated on the water-bath for 30 minutes. Ten successive treatments of this type removed approximately the same amount of lead (about 7 mgrms.) for each extraction. The lead was determined by Sudenorf and Penndorf's modification of Winkler's colorimetric method (*id.*, 1923, 45, 361), and by the volumetric chromate method. After extraction a white, water-soluble efflorescence containing carbonate, sulphate, acetate and aluminium, was observed on the enamel. J. G.

Biochemical.

Improved Colorimetric Method for the Determination of Cystine in Proteins. O. Folin and A. D. Marenzi. (*J. Biol. Chem.*, 1929, 83, 103-108.)—The validity of the method of Folin and Looney (*J. Biol. Chem.*, 1922, 51, 427; *ANALYST*, 1922, 47, 359) for the determination of cystine in protein hydrolysates has been re-examined. The method has been criticised at different times, and accurate cystine determinations have become increasingly important. The Folin-Looney method as it stands in the literature has two known defects. It does not provide for the removal of molybdate (and phenol reagent) from the uric acid reagent, and thus it is possible that some tyrosine is included in the cystine determinations; for the same reason, the reagent gives an uncomfortably large blank with the sodium sulphite used for the preliminary reduction of cystine to cysteine. A third defect, discovered in the course of the work, is that cysteine reacts less rapidly with the uric acid reagent than does uric acid. To obtain complete reaction with the cysteine necessitates the addition of much more of the uric acid reagent than was originally used. A uric acid reagent entirely free from phenol reagent has now been prepared by the authors (*J. Biol. Chem.*, 1929, 83, 109-113), and with this phosphotungstic acid reagent the influence of tyrosine is entirely eliminated, and also the third defect is remedied. By the addition of the sulphite to the acid cystine solution, that is, before instead of after the carbonate, the amount of 20 per cent. sulphite used is reduced from 10 c.c. to 2 c.c., and thus the blank produced by the sulphite becomes negligible. On the basis of these improvements it has been found possible to obtain a true range of proportionality between colours obtained from different amounts of cystine between 10 mm. and 40 mm. when the standard is set at 20 mm. The blue solutions are diluted with 3 per cent. sodium sulphite solutions instead of water to avoid a bleaching effect. The sum total of all these refinements of the Folin-Looney method for the determination of cystine is so great that there can scarcely be any comparison in the dependability of the results obtained by the two forms of the method. The method is described in detail. Samples of casein, gliadin, edestin, zein, egg albumin and serum albumin have been examined for their cystine content; the results given obtained by the new method are higher than the figures obtained by the original method except in the case of gliadin, the figures for which are slightly lower. P. H. P.

Determination of Carbon Monoxide in Blood. W. M. M. Pilaar. (*J. Biol. Chem.*, 1929, 83, 43-50.)—Most of the known methods for the quantitative determination of carbon monoxide in blood are briefly discussed and criticised. The method of Cohen Tervaert (*Biochem. J.*, 1925, 19, 300) has now been modified and converted into a micro method. In the original method the carbon monoxide is liberated by the addition of potassium ferricyanide in a vacuum. It then reacts with iodine pentoxide, heated to 150° C., according to the reaction— $I_2O_5 + 5CO \rightarrow 5CO_2 + I_2$, and the iodine liberated is absorbed in a potassium iodide solution and titrated with 0.01 N thiosulphate solution from a micro burette.

This procedure is subject to the following criticisms: (1) The amount of blood necessary for a determination is 10 c.c., and necessitates venepuncture, (2) the large Peligot tubes of the apparatus seem unsuitable, especially for taking up the iodine, (3) some of the iodine is absorbed by the rubber stoppers and tubing, and (4) the concentration of the potassium iodide solution recommended (0.5 per cent.) is too low, and results in low figures in cases of high carbon monoxide content. The modified apparatus for the new method is shown in a figure and described, and details of the method are given. Only 1 c.c. of blood, which can be obtained from a finger tip or ear lobe, is necessary for a determination. Tables show the recovery of carbon monoxide from air and from blood by this method. The method is being applied to the examination of blood from people who, as a result of their occupation, are exposed to carbon monoxide. Motor car drivers and garage workers are the chief cases. Some of the results obtained are given. It is stated that 1 c.c. of blood from an adult with an average haemoglobin content can contain a maximum of about 0.250 c.c. of carbon monoxide. Whenever 20 to 30 per cent. of this is present, rather serious acute symptoms can be found. P. H. P.

Quantitative Determination of Bile Acids by means of a New Colour Reaction and Monochromatic Light. R. Gregory and T. A. Pascoe. (*J. Biol. Chem.*, 1929, **83**, 35-42.)—The Pettenkofer reaction (*Ann. Chem.*, 1844, **52**, 90) was studied and found unsuitable for the quantitative determination of bile acids in pure solutions, and unreliable for even qualitative work on body fluids. A new colour reaction for the determination of bile acids is described which is more specific and more accurate than the Pettenkofer procedure. When to a dilute bile acid solution are added 34 per cent. of sulphuric acid by volume and 0.05 per cent. of furfural by volume, and the mixture is heated for 30 minutes at 65°C., a pure blue colour results, which is different from any that has been reported in the literature. The blue-coloured compound is stable for 2 to 3 hours, perfectly reproducible, and quantitative in character; *i.e.*, it conforms to Beer's law. The reaction which gives the blue colour is called the Gregory reaction. Portions of sodium glycocholate solutions of known concentration (0.1 and 0.2 mgrms. per c.c.) were measured into test-tubes with a calibrated micro burette, made up to 1 c.c. with distilled water, 6 c.c. of 45 per cent. sulphuric acid solution were added, then 1 c.c. of 0.3 per cent. furfural solution, and the tubes were loosely stoppered and set in a water-bath at 65° C. for 30 minutes, and then compared with a standard solution. Very good results were obtained, but in all cases when the concentration was less than that of the standard there was a positive error, whilst a greater concentration than the standard always gave a negative error. Various substances other than bile acids that give a positive Pettenkofer reaction, including glycine, taurine, cholesterol, lanolin, lecithin, cephalin and oleic acid, gave negative results when tested in this way. Since these include the substances that might be present in blood, and as an alcoholic extract of normal blood does not give the Gregory reaction, the test is suitable for the determination of bile acids in an alcoholic extract of blood. In the presence

of bile pigments simple colorimetric analysis failed, and a spectrophotometric study of the blue colour of the Gregory reaction was therefore made. A marked absorption band was shown, the centre of which was at 6200 Å. A new, simple and inexpensive apparatus for obtaining monochromatic light of this wave-length (about 6200 Å) for illumination of the colorimeter was devised for use in the study of the bile acid content of bile and blood. Results show that by means of the new colour reaction and monochromatic light it is possible to determine bile salts in bile quantitatively, which is not possible with the Pettenkofer reaction. In no instance did the presence of the relatively large amounts of bile pigment interfere with the comparison of the colour in the bile solutions with that of standards prepared from pure sodium glycocholate. No bile salts were found in two trials with about 5 litres each of normal ox-blood. These results are contrary to those of Roundtree, Greene and Aldrich (*J. Clin. Inv.*, 1927, 4, 545), who reported the presence of 2.5 to 6 mgrms. of bile salts per 100 c.c. of normal human blood. Bile acids or their salts are insoluble in ordinary fat solvents, but readily soluble in the solution of fat in these solvents.

P. H. P.

Distribution of Copper in Blood. C. A. Elvehjem, H. Steenbock and E. B. Hart. (*J. Biol. Chem.*, 1929, 83, 21-25.)—Some samples of haemoglobin have been analysed for copper; no studies have previously been made directly on this pigment, and the possibility of the presence of copper in the molecule is the first question to be answered in the determination of the function of copper in haemoglobin building. Two samples of horse blood gave 0.034 mgrm. of copper and 0.019 mgrm. of copper per grm. of dry haemoglobin respectively; thus on the assumption that there is 1 atom of copper per molecule of haemoglobin, the smallest calculated molecular weights are 1,870,588 and 3,344,368 respectively, both of which are many times the accepted value. The sample purified to the largest extent contained the smallest amount of copper. The original work showing the importance of copper as a supplement to iron for haemoglobin building was conducted with rats, and therefore similar analyses have also been carried out on haemoglobin from rat blood, prepared according to the method of Heidelberger (*J. Biol. Chem.*, 1922, 53, 31). An average of 0.015 mgrm. of copper per grm. of oxyhaemoglobin was obtained, from which the calculated molecular weight is 4,240,000. Therefore, if the molecular weight of haemoglobin is accepted as 16,700 (the early figure) or 66,800, as recently reported by Svedberg and Fahraeus (*J. Amer. Chem. Soc.*, 1926, 48, 430), then the haemoglobin of rat blood does not contain copper as part of its molecule. The copper content of horse blood has been determined and found to be approximately 0.05 mgrm. of copper per 100 c.c. of blood. The corpuscle fraction of blood, whether prepared by centrifuging oxalated blood, or defibrinated blood, contains the largest portion of the copper. Further work must be done to establish the exact relation of these minute traces of copper and the blood.

P. H. P.

Effect of Diet on the Copper Content of Milk. C. A. Elvehjem, H. Steenbock and E. B. Hart. (*J. Biol. Chem.*, 1929, 83, 27-34.)—A recent publication by Hart, Steenbock, Waddell and Elvehjem (*J. Biol. Chem.*, 1928, 77,

797) demonstrated the importance of copper as a supplement to iron in the prevention of anaemia in rats kept on a diet of whole cow's milk. Experiments have now been carried out to determine the actual amount of copper present in cow's milk, to detect variations in the copper content which might appear in milk produced under different conditions, and to show whether the copper content of cow's milk can be increased appreciably by the addition of copper salts to the normal ration of a cow. Different workers have reported wide variations in the time required for rats to become anaemic on a whole milk diet; it was hoped by this work to show whether the copper content of milk can be varied enough to account for these differences. Analyses are presented of samples of milk from individual cows and goats which have been fed on a normal ration or one supplemented with copper, and the analyses of composite samples of milk obtained from herds of cows located in various sections of the United States. The results show that milk produced by cows on a normal ration contains about 0.15 mgrm. of copper per litre. This figure is considerably lower than most figures for raw milk reported in the literature. The authors believe that many of the high figures reported are due to copper contamination during the process of analysis, especially from the dishes used for the ignition of the milk. The copper content of cow's milk cannot be increased by feeding the cows with sufficient copper sulphate to increase the copper intake 5-fold. Samples of cow's milk collected from thirteen herds located in different states showed very slight differences in copper content. The figures ranged from 0.123 mgrm. per litre for the milk from North Carolina to 0.184 mgrm. per litre for the milk from Texas. The copper content of goat milk was not increased when the copper content of the ration was increased five to ten-fold. Further, limited numbers of analyses for copper did not indicate a decidedly lower amount of this element in goat milk as compared with cow's milk; this is contrary to the results of Quam and Hellwig (*J. Biol. Chem.*, 1928, **78**, 681; *ANALYST*, 1928, **53**, 542). It is concluded that the difference in the rate of anaemia production in rats on whole milk diets, reported by different investigators, cannot be due to a variation in the copper content of the milk when produced, but rather to the contamination of the milk after production, or to unknown sources of copper supply during the different periods of the rat's life.

P. H. P.

Iron in Nutrition. IX. Further Proof that the Anaemia Produced on Diets of Whole Milk and Iron is due to a Deficiency of Copper. J. Waddell, H. Steenbock, C. A. Elvehjem and E. B. Hart. (*J. Biol. Chem.*, 1929, **83**, 251-260.)—It was shown recently by the authors (*J. Biol. Chem.*, 1928, **77**, 777, 797) that copper in varying amounts was present in all their fractions which cured the anaemia developed in rats on a diet of cow's whole milk and iron. However, the question arose as to whether or not copper was the only element occurring in the preparations which could supplement iron in the cure and prevention of the particular type of anaemia being studied, and results are now presented of experiments which have been carried out, and which show the specificity of copper in this respect. The authors used a variety of preparations, and compared them

all on the basis of their copper content, so that any other substance (or substances), *organic* or *inorganic* in nature, that was potent in haemoglobin regeneration would reveal its presence, especially when the copper intake was very low. Several liver preparations, hydrogen sulphide fractions of the acid extracts of the ashes of two of them, and copper as a solution of copper sulphate, all on the same levels of copper intake, were shown to serve equally well as supplements of a basal diet of whole milk and iron, to cure the nutritional anaemia produced by the basal diet. This is, therefore, additional and convincing proof that the deficiency of this basal diet is *inorganic* in nature, and that this inorganic deficiency is copper only.

P. H. P.

Effect of Heat on Milk. (a) On the Coagulability by Rennet, and (b) On the Nitrogen, Phosphorus, and Calcium Contents. E. C. V. Mattick and H. S. Hallett. (*J. Agric. Sci.*, 1929, 19, 452-462.)—Since the addition of a solution of a calcium salt to pasteurised milk permits of the formation of an almost normal curd by the action of rennet, it appears that the heating affects mainly the calcium salts of the milk. The experiments now described show that milk which has been heated for 30 minutes to temperatures ranging from 105° to 209° F. differs from raw milk in its reaction towards rennet in all cases. No change is observed in the diffusibility of the nitrogenous substances of the milk as a result of such treatment, but the diffusibility of the phosphorus content appears to be reduced at 175° F., and that of the calcium content is diminished markedly at 125° F.

T. H. P.

Enzymic Conversion of Uric Acid into Allantoic Acid. R. Fosse, A. Brunel and R. de Græve. (*Compt. rend.*, 1929, 189, 213-215.)—Many leguminous seeds are able to transform uric acid into allantoic acid, this change being effected by means of two enzymes. The first, an oxydase, like animal uricases, converts the uric acid into allantoin, which then fixes water under the influence of the second enzyme.

T. H. P.

Further Studies of the Chemical Nature of Vitamin A. J. C. Drummond and L. D. Baker. (*Biochem. J.*, 1929, 23, 274-291.)—The unsaponifiable fraction from 125 gallons of high-quality medicinal cod-liver oil was submitted to fractional distillation at pressures of about 0.01-2 mm., but it was not found possible thereby to separate vitamin A. After removal of most of the cholesterol fractionating caused decomposition, with considerable loss of the vitamin. Separation of the constituents of the fraction by the preparation of phthalates or substituted phthalates was also impracticable, nor could information as to their nature be obtained by reduction with hydrogen in the presence of catalysts. The same difficulties were encountered with the unsaponifiable fraction from sheep-liver fat, and here decomposition was, at least partly, due to the presence of a highly unsaturated hydrocarbon somewhat resembling squalene. The unsaponifiable fractions of Greenland and Japanese shark liver oils consisted largely of selachyl, batyl, chimyl and oleyl alcohols, and distillation of the fractions was accompanied

by comparatively little destruction of the vitamin, probably owing to the small proportion of complex alcohols and hydrocarbons of the terpene series. It is concluded that vitamin *A* is present in such small proportions (probably less than 1 per cent.) in the unsaponifiable fraction that chemical means of separation are unlikely to succeed unless some characteristic derivative possessing properties suitable for isolation should be discovered. In support of this view, recognisable substances to the amount of 90–95 per cent. of the whole material were isolated from the unsaponifiable fraction of Japanese shark-liver oil, and, so far as could be ascertained, the residue consisted to a large extent of the same substances in less pure condition. The structure for chimyl alcohol as a monoglyceryl ether of cetyl alcohol has been confirmed.
D. G. H.

Vitamin *B* Content of Polished Rice Koji. R. Takata. (*J. Soc. Chem. Ind. Japan*, 1929, 32, 188B.)—Rats fed with polished rice koji as the sole source of the vitamin attained 105 to 142 grms. in weight in 3 months, when growth stopped and their body weights began to decrease. Those fed with polished rice upon which *Aspergillus oryzae* had not grown died within 2 months. Pigeons fed with polished rice koji died in 30 to 41 days, whereas those fed with polished rice died in 23 to 35 days. It would therefore appear that polished rice koji contains very little vitamin *B*.
R. F. I.

Agricultural.

Analysis of Tomato Plants, I. O. Owen. (*J. Agric. Sci.*, 1929, 19, 413–432.)—In order to evaluate the part played by phosphates in tomato culture, the plants subjected to various treatments have been analysed for potash, phosphoric acid and nitrogen. Immediately after collection the material was freed from foreign matter, the green weight being recorded and the sample dried at 98–100° C. to constant weight, usually attained after 12 or 16 days. With old plants the dried stalks were cut up, the whole of the sample being ground in a porcelain mortar or a hand mill to pass a fine sieve. The nitrogen in 0.75–1 grm. of the dry tissue was determined by the Kjeldahl method, the amount of nitrate and other nitrogen to which this method is inapplicable being apparently negligible. For the determination of the ash, 2–3 grms. of material were heated at low redness to constant weight, the ash of foliage and stems being of a uniform grey colour. The fruit gave dark grey or black ash, but the amount of carbon present proved negligible. For the determination of potash and phosphoric acid, the weighed ash was dissolved in 10 per cent. hydrochloric acid, hydrogen sulphide being evolved with the ash of green tissue. The acid solution was heated to boiling and filtered into a measuring flask, the cold filtrate and washings being made up to volume. Aliquot parts were measured into silica dishes, and sufficient baryta solution to precipitate the sulphates, and also some calcium carbonate, were added. After the silica had been rendered insoluble, potassium was determined in the hot aqueous extract of the residue by the perchlorate method, and phosphoric acid in

the acid extract by precipitation as ammonium phosphomolybdate and weighing as the blue anhydride.

The results obtained show that the needs of the tomato plant for phosphates as a direct nutrient are low, but it is possible that lack of phosphate may reduce the intake of potash—supplied only as sulphate—and affect the flavour of the fruit. With unmanured plants the fruit is of inferior quality, but its weight is 2.6 times that of foliage and stems; with manured plants, which have a higher ash content, this ratio is 1.6. The actively growing parts of the plant are richest in the three nutrients, and the determination of these in grms. per plant for manured and unmanured plants, respectively, gave: Potassium oxide, 18.22 (2.775); phosphoric anhydride, 2.028 (0.9895); nitrogen, 9.324 (4.922). The percentage composition of the fresh fruit from manured (unmanured) plants was: Water, 93.5 (94.9); potassium oxide, 0.3237 (0.0556); phosphoric anhydride, 0.0491 (0.0355); nitrogen, 0.1591 (0.1769).

T. H. P.

Cobaltinitrite Volumetric Method of Determining Potassium in Soil Extracts. G. Milne. (*J. Agric. Sci.*, 1929, 19, 541–552.)—The platinichloride and perchlorate methods often yield unsatisfactory results when applied to the determination of the small proportions of potassium in soils. The cobaltinitrite method also presents difficulties, and in order to overcome these the following modified procedure has been devised. The reagents used are: Sodium nitrite, 100 grms. per litre; sodium chloride, saturated solution; cobalt chloride ($6\text{H}_2\text{O}$), 100 grms. per litre; acetic acid, 100 grms. per litre; sodium sulphate, 25 grms. per litre; glass dust, passing a 100-mesh sieve, in suspension in water; standard potassium permanganate solution, conveniently 0.05 *N*; standard oxalic acid, conveniently slightly stronger than 0.05 *N*, and containing 50 c.c. of sulphuric acid per litre. Freedom of the reagents from potassium must be ensured by satisfactory blanks. The solution prepared for analysis should be neutral and free from ammonium salts and organic matter, and the analysis should not be conducted where ammonia is being used. Aliquot parts representing up to 0.05 gm. of potassium oxide (requiring about 120 c.c. of 0.05 *N* permanganate) may be taken for the quantities of reagents specified, but from 0.005 to 0.025 gm. is most convenient.

The solution for analysis is reduced to about 10 c.c. in a 3-inch evaporating dish, 10 c.c. of the sodium chloride solution, 10 c.c. of the cobalt chloride solution, and 15 c.c. of the sodium nitrite solution being added in order, and the whole mixed with a short glass rod, which is left in the basin. The mixture is evaporated on a steam-bath to stiff pastiness or hard dryness, being well stirred occasionally, especially towards the end of the evaporation, to work the crystalline crusts into the liquid. After cooling (the analysis may be interrupted here), 10 c.c. of 10 per cent. acetic acid are well stirred in to assist solution of the excess of reagents and sodium chloride. After 15 minutes 10 c.c. of water are mixed in and the whole filtered through a small Gooch crucible charged with a disc of No. 40 Whatman paper, well pressed down at the edges and covered with a layer of the finer particles

of the glass dust. The precipitate is washed by decantation with 2.5 per cent. sodium sulphate solution, transferred to the crucible, and washed six or eight times with the same wash liquid; total washings need not exceed 25 c.c. (the analysis may be interrupted here). Allowing for an excess of at least 10 c.c., a measured quantity of 0.05 *N* permanganate is diluted and heated to boiling, about 10 c.c. of dilute sulphuric acid added from a burette, and the solution again boiled and removed from the flame. The precipitate in its crucible is immediately added and stirred round well, and the beaker covered and left for 10 minutes. After 2 or 3 minutes hydrated manganese dioxide separates and if left for longer than 15 or 20 minutes this may be slow in redissolving later. A measured volume of the standard oxalic acid, sufficient to give a perfectly clear solution, is now added and, after removal of the crucible, the excess of oxalic acid is titrated with permanganate. A complete blank analysis (better two or three) should be made for each new set of reagents and may with advantage be repeated from time to time during a long series of analyses: 1 c.c. of 0.05 *N* permanganate corresponds with 0.000415 gm. of K_2O .

When this method is applied to citric acid soil extract, the organic matter may be removed either (1) by evaporation with nitric acid, followed by gentle ignition, the aqueous extract of the finely powdered residue being used for the analysis, or (2) by ignition without nitric acid, silica being then removed, and the residue again ignited and extracted with water. Either procedure gives 96–97 per cent. recovery of added potassium salt. Analyses of ammonium chloride extracts gave unsatisfactory results, and attention is directed to the need for a convenient means of destroying large amounts of ammonium salts in cases where an appreciably volatile constituent is to be estimated in the residue. T. H. P.

Detection of Castor Beans in Feeding Stuffs. M. Wagenaar. (*Z. Unters. Lebensm.*, 1929, **57**, 413–418.)—The detection of castor beans (*Ricinus communis minor* or *major*) in cattle foods is of importance on account of the poisonous nature of the toxalbumin. Robert's biological method (*Chem. Ztg.*, 1913, **37**, 1282) in which an anti-ricin serum is used, is stated to be capable of detecting 0.1 per cent., but the blood agglutination method, though very sensitive, is easily upset by other constituents. Microscopically the bean is identified by a layer of short, black or dark-brown, 4- or 8-sided, slightly curved prismatic palisade cells, under a stratified spongy parenchyma immediately beneath the epidermis. They are very resistant to most reagents, but strong nitric acid readily separates them. In polarised light a fine, bright characteristic fringed edge is seen, and the cells, which are doubly refracting, show pale blue longitudinal and yellow latitudinal interference colours. To determine the proportion of castor beans from the area of these cells 1 gm. of the defatted sample is pulverised in an agate mortar to separate the calcium silicate. The fragments (less than 0.5 sq. mm. in size) are heated for 1 hour on the water-bath in a wide-necked flask with 4 grms. of potassium chlorate and 50 c.c. of 2 *N* hydrochloric acid, when the chlorine liberated serves to separate the palisade cell, which fall to the bottom. After the addition

of 50 c.c. of 4 *N* sodium hydroxide solution and a further hour on the bath, the liquid is decanted, the cells concentrated in a centrifuge, and suspended in a viscous medium such as invert sugar syrup prepared from 70 grms. of sucrose, 30 grms. of water and 1 gm. of citric acid. A drop is placed on a microscope slide (2.8×2.3 cm. \times 0.5 mm.) so that 1 sq. mm. fills the field, and weighed, and the total surface of the cells measured. The cells from 1 gm. of sample have an area of 1500 sq. mm. Candle nut (*Aleurites triloba* or *moluccana*), which is little used in Europe, has similar cells which, however, occur in blocks and are bigger and seldom curved, and lack the characteristic edge of the castor bean cells. Up to 1.5 per cent. of castor bean was added to linseed, arachis and rape cakes and determined by this method, with an error of 0.05 to 0.15 per cent.

J. G.

Organic Analysis.

Tests for Phenols involving the use of Hydrogen Peroxide. A. H. Ware. (*Pharm. J.*, 1929, 123, 15.)—The hydrogen peroxide is either used as the principal reagent, or to hasten, accentuate or alter the effect of the principal reagent, such as dihydroxyacetone or formaldehyde. In one method the reagent consists of 1 c.c. of a 10 vol. solution of hydrogen peroxide made up to 50 c.c. with concentrated sulphuric acid, and more distinctive results are obtained than in the second method, where one drop of the aqueous solution of hydrogen peroxide is added to the phenolic solution in the strong acid. Apparently specific results are described for the catechins, catechol, phloroglucinol, resorcinol, thymol, and gallic acid. Hydrogen peroxide alone enables a distinction to be made between carbolic acid and the cresols, and between phloroglucinol, orcinol and resorcinol. The test for catechins may be successfully applied to the identification of gambier.

D. G. H.

A Reaction of Resorcinol and a New Coloured Indicator. L. Bey and M. Faillebin. (*Comptes. rend.*, 1929, 188, 1679–1681.)—Resorcinol reacts with aqueous ammonia solution in the presence of certain cations to give a blue coloration, and the colour is also produced in the presence of lead acetate or stannic chloride. The reaction is an oxidation, and the cation acts as a catalyst. The blue colour is due to an unstable combination of a colouring matter with one or more constituents present in the solution, and when isolated is irreversibly converted in ammoniacal solution to another blue colouring matter. The first colour is red in acid solution, green in a solution of P_H 9.18, and in ammoniacal solution of a higher P_H value is transformed into the second blue colouring matter, which is rose-red in acid solution. These colouring matters may be isolated by extraction of the acid solution with a solvent such as amyl alcohol, and subsequent shaking with a buffer solution of known P_H , preferably within the range of the indicator. The red-blue indicator is obtained unless the shaking is in an acid medium, in which case the red green indicator results. The P_H range for the red-blue indicator is 4.3 to 5.9, the intermediate tints being violet.

D. G. H.

Micro-Method for Determining Semicarbazones and its Application to the Analysis of Ketones. R. P. Hobson. (*J. Chem. Soc.*, 1929, 1384–1385.)—Solutions of semicarbazone or semicarbazide are hydrolysed if boiled under a reflux condenser with 15 per cent. of hydrochloric acid and 5 per cent. of mercuric chloride for 8 and 6 hours, respectively, the function of the latter being to oxidise the hydrazine formed and so prevent the production of ammonia by interaction with organic substances (*e.g.* sucrose, free ketones):—(1) $\text{NH}_2\text{CO.NH.NH}_2 + \text{H}_2\text{O} = \text{NH}_3 + \text{CO}_2 + \text{N}_2\text{H}_4$, (2) $\text{N}_2\text{H}_4 + 2\text{HgCl}_2 = \text{N}_2 + 2\text{Hg} + 4\text{HCl}$. If about 10 mgrms. of sample are used, the ammonia may be determined by means of Pregl's micro method, the liquid being made alkaline with a mixture of equal volumes of 40 per cent. sodium hydroxide and saturated sodium thiosulphate solutions. The latter serves to decompose the mercury and ammonium complex. The method has also been applied to ketones which may be converted quantitatively into semicarbazones, though excess of semicarbazide reagent must first be removed by precipitation of the semicarbazone with water, or by extraction of the semicarbazide by washing it with water from the evaporated mixture, or by extracting the residue with ether and shaking the ethereal solution with water. J. G.

Inorganic Analysis.

The Benzidine Colour Reaction of Japanese Acid Clay. N. Kameyama and S. Oka. (*J. Soc. Chem. Ind. Japan*, 1929, 32, 87B.)—The benzidine colour reaction was carried out in the complete absence of oxygen and still gave a positive result. The oxidising constituent of the clay can be removed by boiling it with 6 N hydrochloric acid for 30 hours. Evidence was found that Japanese acid clay also exerts an oxidising effect, though to a minor degree, by acting as a catalyst in the presence of oxygen. R. F. I.

Synthetic Japanese Acid Clay. N. Kameyama and S. Oka. (*J. Soc. Chem. Ind. Japan*, 1929, 32, 99B.)—The oxidising power, in which property the previously described synthetic clay (*ANALYST*, 1929, 65) was lacking, is supplied by adding 0.1 per cent. of manganese dioxide. This product then possesses all the known properties of the natural clay, though in some cases to a somewhat less degree. The blue coloration on contact with liver oil was less pronounced than that produced by the Japanese acid clay. (*Cf. ANALYST*, 1927, 553, 559.) R. F. I.

Genesis of Japanese Acid Clay. K. Kobayashi and K. Yamamoto. (*J. Soc. Chem. Ind. Japan*, 1929, 32, 174B.)—The authors have observed that acid clay is exclusively found along an intrusion of liparite through the Pliocene. The view is put forward that Japanese acid clay is a decomposition product of soda felspar and sodium silicate interposed between pre-tertiary strata and the liparite, the decomposition being effected by upgushing gases (carbon dioxide, sulphur dioxide, hydrogen sulphide, and steam), and a gel of hydrated aluminium silicate being formed. R. F. I.

Physical Methods, Apparatus, etc.

Testing Seeds, etc., under the Quartz Mercury Vapour Lamp. A. Niethammer. (*Z. Unters. Lebensm.*, 1929, 57, 354–358.)—In certain cases the mercury vapour lamp may be used to distinguish fresh and sound seeds from old and damaged material, but it can be considered only as a guide, particularly when applied to identify seeds of different types. Fresh intact *Cannabis sativa* and *Ervum lens* give green colours, and old samples a matte-white. For *Lupinus albus* a grey brown colour is obtained, varying towards a yellow shade in old samples. *Pisum sativum* shows a lilac luminescence with red stripes which are absent from old samples, whilst *Phaseolus vulgaris* and *Vicia sativa* are lilac and bright green, respectively, if fresh, but show no colour if old. *Vicia faba* and *Linum usitatissimum* vary from dark blue or lilac to pale yellow according to age. *Agrostemma githago*, *Sinapis alba*, *Brassica nigra*, *Ricinus communis*, *Secale cereale*, *Triticum sativum*, *Hordeum vulgare* and *Fagopyrum* all give lilac colours, new and old samples being indistinguishable. Walnut, hazel nut and almond give lilac colours when fresh and yellow when old, and coconut a characteristic lilac which is absent from old samples (*cf.* Popp, *ANALYST*, 1926, 51, 540). J. G.

Reviews.

THE CHEMISTS' YEAR BOOK, 1929. Edited by F. W. ATACK, D.Sc., F.I.C.
Pp. 1185 and Index. Manchester: Sherratt & Hughes. Price 21s.

The present edition of this work is the fourteenth to be published, and the annual appearance of the volume affords every indication of its utility. No new section has been included in the new volume, but the chapters on "Dairy Chemistry" have been re-written by Elsdon and Stubbs, two well-known authorities in this country. The number and variety of subjects with which the work deals is very large, each section having an importance dependent on the nature of the work of a particular chemist. The work is convincing of the marked progress which has been made in all domains of chemistry, and a glance at the pages of the volume is impressive, as it shows the almost innumerable subjects with which the chemist has to deal.

The article on "Qualitative Analysis. Dry-way Tests" occupies rather more than nine pages, but who would dare to suggest their suppression? Do they not convey the mind back to early schooldays, when troubles of a chemical nature were very real? The forward trend of science has, however, left most laboratories without "a charcoal block with a clean cavity in which to heat a substance in an oxidising flame," but this can be remedied.

The British Pharmacopoeia limits for lead and arsenic are set out in a convenient tabular statement, but, somewhat unfortunately, the prescribed tests of the U.S.P. are not given, but only a reference to Part II of that work which contains the tests. The U.S.P. is not always available.

The section on "Dairy Chemistry" states that the condition of sour milk may be improved by the addition of ammonia. It should be noted that the addition of ammonia to sour milk does not prevent the loss of solids on evaporation, and that, unless neutralisation has been effected with soda or strontia, the result obtained for total solids will be low.

The section devoted to "Agricultural Chemistry" has been written by no less an authority than Sir E. J. Russell, F.R.S. He deals very ably with the analysis of soils, and then passes on to the examination of fertilisers and, subsequently, to feeding stuffs. Unfortunately, the official methods of analysis given for both fertilisers and feeding stuffs are those which were contained in the Fertilisers and Feeding Stuffs Regulations, 1908; these were superseded by Regulations dated May, 1928. The processes given are, therefore, now, not necessarily official, and, further, the chapter obviously contains no mention of alternative processes included in the more recent Regulations. It is most desirable that the methods of analysis for feeding stuffs should be brought up to date without delay. The revision of the processes relating to the determination of oil and fibre, in particular, is most important, because of the differences in results which may be obtained by the old and new methods.

The only portion of the book which appears to remain stationary in length is the index. Somewhat unfortunately, the index only extends to sixteen pages, as it did twelve years ago. To a busy man, the utility of any work must depend to a large extent on the ease with which information can be run down in the text. The index might well be made more complete.

The work claims the highest commendation, and, generally, the analyst requiring information would not appeal to its pages without profit.

F. W. F. ARNAUD.

PHOTOMETRIC CHEMICAL ANALYSIS. Vol. II. NEPHELOMETRY. By JOHN H. YOE, Ph.D., with contributions by HANS KLEINMANN, M.D., Ph.D. Pp. xvi+337. London: Chapman & Hall, Ltd. Price £1 2s. 6d. net.

This is the complementary volume to the one on "Colorimetry" reviewed in *THE ANALYST* last March, and like the companion volume it is well produced. The subject is new, so much so that, save for some suggestive preliminary work by Mulder in 1859, its foundations were not laid until 1894, when Stas and T. W. Richards independently investigated its possibilities in atomic weight work. To the latter belongs the honour of having established the method, and to Kober the credit for its further development since 1912; precision instruments belong to the present decade. Thanks are due to the author for having narrated the history in

detail, while memory is fresh, and also for having entered into minutiae of the instruments and their operation. This is good in a first general treatise, but in the next edition, which there is good reason to anticipate, the same information could be imparted more concisely to the advantage of the reader. A tendency to prolixity is evident throughout the book.

A far more serious weakness is in the arrangement of the work. The reader has presented to him the several nephelometers, the construction, operation and care of precision instruments, the theory of nephelometry, and is lead on to the practice of the art without being made acquainted with the general principles of the subject. It is not until he reaches Chapter V on the theory that the reader becomes aware of how the incident light is projected into the liquid, save only as far as general intelligence and experience assist him. A good general introduction describing the fundamental principles, a typical nephelometer, how to use it and the purposes to be served in academic and technological practice, would have made the following chapters much more easily readable.

The text fails of good expression in places; for example: "The theory of nephelometry may be defined as an explanation of the scattered visible light coming at right angles from an illuminated column of suspended substance and of the relationship between the intensity of scattered or reflected light and the concentration of the suspended particles." "The property of suspended substances scattering light is called Tyndall effect." (Page 48.)

On comparing the list of elements and substances to be determined by nephelometry in Vol. II with that of those to be quantified colorimetrically in Vol. I, one is impressed by so little overlapping. The six chapters on Inorganic Elements refer to Ammonia, Arsenic, Calcium, Chlorine, Phosphorus, and Sulphur; and the eleven chapters on Organic to Acetone, Amylase, Dichloro-Ethylsulfide, Fats, Oils and Fatty Acids, Lipase, Nucleic, β -Oxybutyric Acid, Pepsin, Proteins, Purine Bases and Trypsin. An attractive chapter to the practising analyst is the one on Ammonia, which describes how the nitrogen in an organic substance may be determined by the usual Kjeldahl digestion in Sulphuric Acid followed by simple dilution, the addition of reagents, and matching the cloud against that produced in a standard Ammonium Sulphate solution.

Other chapters which make a similar appeal are those referring to Pepsin, Proteins and the like. Simple nephelometric methods may replace the difficult chemical separations; thus "From two to three days are required for the determination of casein, globulin and albumin in milk when it is done by the usual technique, whereas with the nephelometric method it can be done in twenty to thirty minutes." (Page 256.)

The author's very carefully prescribed directions indicate the need for close attention to detail as a necessary condition for obtaining precise results, but this should not discourage a wide use of the method for both precise and approximate determinations according to requirements; no doubt approximate work will meet

the needs of much control work, and prove very convenient in practice. The author would have strengthened his advocacy of so new a method had he given more information as to how results so obtained compare with those following from the better known methods.

The volume closes with a good classified bibliography, which is better arranged than is that in Vol. I.

S. JUDD LEWIS.

Publications Received.

INDEX TO THE LITERATURE OF FOOD INVESTIGATION. No. 1. Department of Scientific and Industrial Research. Compiled by AGNES ELIZABETH GLENNIE, B.Sc. H.M. Stationery Office. Price 2s. net.

Historical review of earlier papers—Classified summary of more recent papers and patents: —I, Meat; II, Pig flesh; III, Poultry and game; IV, Fish; V, Eggs; VI, Dairy produce; VII, Fats and oils; VIII, Fruit and vegetables; IX, Grain, crops and seeds; X, Theory of canning; XI, Theory of freezing and chilling; XII, Bacteriology; XIII, Mycology; XIV, Engineering; XV, Miscellaneous.

ANNUAL REPORT OF THE MEDICAL OFFICER OF HEALTH FOR LONDON FOR 192
TOGETHER WITH THE REPORT OF THE PUBLIC ANALYST.

ANNUAL REPORT OF THE MEDICAL OFFICER OF HEALTH FOR LEICESTER FOR 192
TOGETHER WITH THE REPORT OF THE PUBLIC ANALYST.

ANNUAL REPORT OF THE CHEMICAL EXAMINER TO THE GOVERNMENT OF MADRAS.

REPORT OF THE DEPUTY CITY ANALYST FOR BIRMINGHAM, FOR THE SECOND
QUARTER, 1929.

HANDBUCH DER BIOLOGISCHEN ARBEITSMETHODEN (ABDERHALDEN). Abt. IV:
QUANTITATIVE STOFFWECHSELUNTERSUCHUNGEN. F.G. BENEDICT. Berlin:
Urban & Schwarzenberg. Price 4 marks.

HYDROGEN IONS. By H. T. S. BRITTON, D.Sc. London: Chapman & Hall.
Price 25s. net.

DIE ROLLE DER ZYKLISCHEN AMINOSÄUREANHYDRIDE IN DER NEUEREN STRUKTUR-
CHEMIE DER PROTEINE. By E. KLARMANN. Berlin: Urban & Schwarzenberg.
Price 9 marks.

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Crayon Portrait of Dr. A. H. Hassall.

A PHOTOGRAPHIC reproduction of a crayon portrait of Dr. Arthur Hill Hassall, drawn in 1853 by J. N. Harland, is published with this issue of *THE ANALYST*.

The original drawing, which measures about 30 by 24 inches, has been presented to the Society by Dr. Hassall's colleague and medical attendant at San Remo, Michael Foster, Esq., M.D., F.R.C.P., to whom a cordial vote of thanks has been voted by the Council.

Arthur Hill Hassall was born in 1817 and died in 1894, and his obituary notice was written by Otto Hehner (see *ANALYST*, 1894, 19, 97). He was the first Vice-President of the Society of Public Analysts.

The Institute of Chemistry has kindly allowed this portrait to be hung in one of its rooms.

The Identification of Apiol.

By JOHN KING, F.I.C.

THE identification of commercial "apiol" is attended by some little difficulty, owing to its variable composition and the lack of reliable information as to the nature of different varieties at present on the market. I have not been able to discover in the existing literature any method which will detect commercial apiols with certainty, and have concluded that a Zeisel determination, carried out on the lines indicated later, is of greater value than any other factor in distinguishing apiol from other naturally occurring oils.

Hilditch and Jones (*J. Soc. Chem. Ind.*, 1927, 46, 174t.) and Walmesley (*Quart. J. Pharm.*, 1928, 1, 388) have recently published work elucidating many difficulties on the subject, and the latter has given a large number of analytical data showing plainly what great differences may be met with in commercial apiols. The analytical constants usually associated with oil analysis, such as specific

gravity, specific rotation, saponification value, etc., are certainly useful, but not quite diagnostic. L. Lutz and G. Oudin (*Ann. Falsif.*, 1910, 295, 335) have suggested analytical limits for different varieties of apiol, together with special tests depending on the action of nitric acid or a mixture of nitric and sulphuric acids on the substance. I have investigated these acid tests and consider that, quite apart from the personal danger in carrying out the tests by this method, the results are apt to be misleading.

The red colour developed on the addition of concentrated sulphuric acid to a few drops of apiol, as described by the British Pharmaceutical Codex and by the French Codex, 1908 edition, is by no means diagnostic, and may, in fact, be quite misleading. Many oily plant extracts will give various shades of red or brown with concentrated sulphuric acid, and in order that the test may be of value, the colour at great attenuation should be compared as to its red component with that given by known specimens. As the colour is affected by the absorption or addition of water, the attenuation should be made with concentrated sulphuric acid. A specimen of German parsley seed oil gave a distinctly red colour at a dilution of 1:30,000, as did also a specimen of Merck's white crystalline apiol. Other specimens of apiol gave somewhat less colour and some very much less. Comparative measurements of the colour produced by several commercial articles were made, in which 0.033 grm. of the apiol was treated with 10 ml. of concentrated sulphuric acid in the cold and stirred until homogeneous. Part of this was then diluted with strong sulphuric acid until a concentration of 1:7,500 was attained, and tests were carried out immediately by means of the Lovibond tintometer, the liquid being contained in a half-inch cell. It was necessary to do this as soon as mixing was complete, as the colour changed on standing, partly owing to absorption of moisture. One specimen, for example, increased its red index number threefold on standing 24 hours. The results, which are given in the table which follows, show how great were the differences of various specimens in colour-producing power.

The absorption spectrum of the colour produced by sulphuric acid may be of service in some cases. The colour showed no definite absorption bands. In specimens, such as Merck's, practically the whole of the absorption occurred at the violet end of the spectrum. Other specimens gave most absorption in the violet region, accompanied by varying amounts in the yellow and green regions. An attenuation in sulphuric acid of about 1:10,000 was found to be the most generally useful.

The rotation of polarised light may give useful negative information at times, but usually that of genuine specimens is so small and the colour so intense that reliable figures are not available. Merck's apiol gave a slight negative reading, and a German parsley seed oil a pronounced negative reading. Chemically pure apiol is optically inactive.

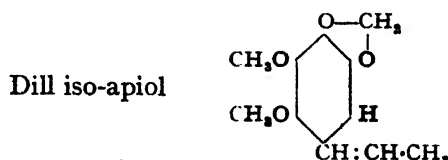
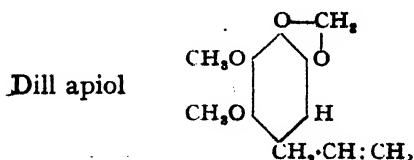
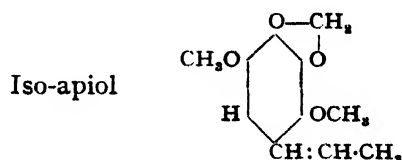
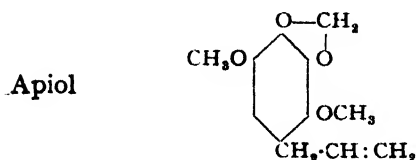
Few oils have a specific gravity greater than unity, the principal commercial ones being those derived from parsley, saffras oil, and those containing eugenol-like bodies, such as oil of cloves. Unfortunately, some of these oils contain

substances having methoxyl groups, the significance of which will be dealt with later, though their odour could hardly be mistaken for parsley derivatives.

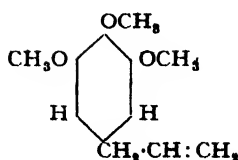
Many naturally occurring oils fall within the refractive index range of 1.480–1.537 reported for apiol, but the refractive index may be useful as a confirmatory test; it has the advantage of requiring very little material. Several other oils containing methoxyl groups, such as matico, dill, elemi, asarum, bay, fennel, arnica and calamus, have refractive indices falling within these limits, and their possible presence should not be lost sight of. Sea fennel oil, for example, contains nearly half its weight of dill apiol, though its specific gravity is somewhat low and it has a strongly positive rotation. The saponification value will show the presence of esters, including, of course, glycerides.

It occurred to me, from a study of the chemical constitution of the substances reported to have been found in apiol, that a more diagnostic constant than any hitherto described would be a Zeisel number, that is, the proportion of volatile iodide obtainable by treatment with hydriodic acid. Furthermore, only, 0.1–0.2 gm. would be necessary, since good specimens give about double their weight of silver iodide. This is a very great consideration when only a few drops contained in gelatin capsules are available, as is often the case in chemico-legal work. The methoxyl content alone cannot be considered to be quite diagnostic, as other naturally occurring substances (including some other essential oils) would give fairly high figures, but these substances are, as a rule, easily differentiated from those of similar composition to apiol. Thus, alcohols (including glycerol), esters (including glycerides), ethers, (including bodies like β -naphthol methyl ether), and other substances contained in some of the well-known essential oils, would possibly give iodine compounds of sufficient volatility to rank as methoxyl-containing compounds under the conditions given later. Generally, the presence of these substances could easily be detected by odour, saponification value, refractive index and specific gravity, and some, such as the glycerides, contribute only a small proportion of iodide. If necessary, some of them could be eliminated by saponification, followed by extracting with low-boiling petroleum spirit the substance required for hydriodic acid treatment.

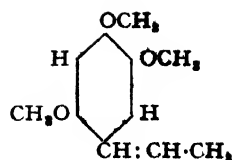
The composition of apiol and related bodies is as follows:—



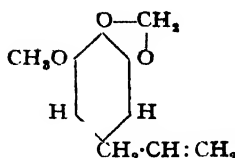
Elemicin



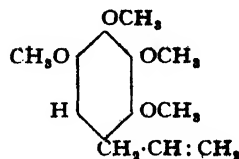
Asaron



Myristicin



Allyl tetramethoxybenzene

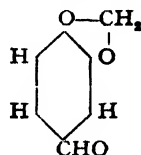


Apiol, myristicin and allyl tetramethoxy-benzene have been found in commercial apiols. Dill apiol has been found in dill oil, elemicin in elemi oil, and asaron in calamus and matico oils.

It may be of interest here to give a list of the principal products from which a fair yield of silver iodide would be given by the Zeisel method:—Apiol, dill, matico, sea-fennel, fennel, elemi, asarum, calamus, cassia, betel, bay, cloves, nutmeg, ylang-ylang, arnica, vanilla, and yara-yara.

The action of hydrogen iodide on glycerides at high temperatures is known to be that of splitting up the molecule, giving eventually isopropyl iodide. There is nothing in the literature, however, to indicate to what extent this goes on quantitatively, and, in view of the large glyceride content of some commercial specimens of apiol, it was necessary to investigate this point under the conditions given later. Pure triolein was chosen for the glyceride, and it was found that only about 50 per cent. of the theoretical yield of silver iodide was obtained under the conditions specified; and this, in view also of the high molecular weight of glycerides, rules out the possibility of glycerides seriously disturbing the results obtained by the modified Zeisel method. The use of alcohol in the preparation of apiol from parsley seed should be borne in mind and a test should be made for its presence.

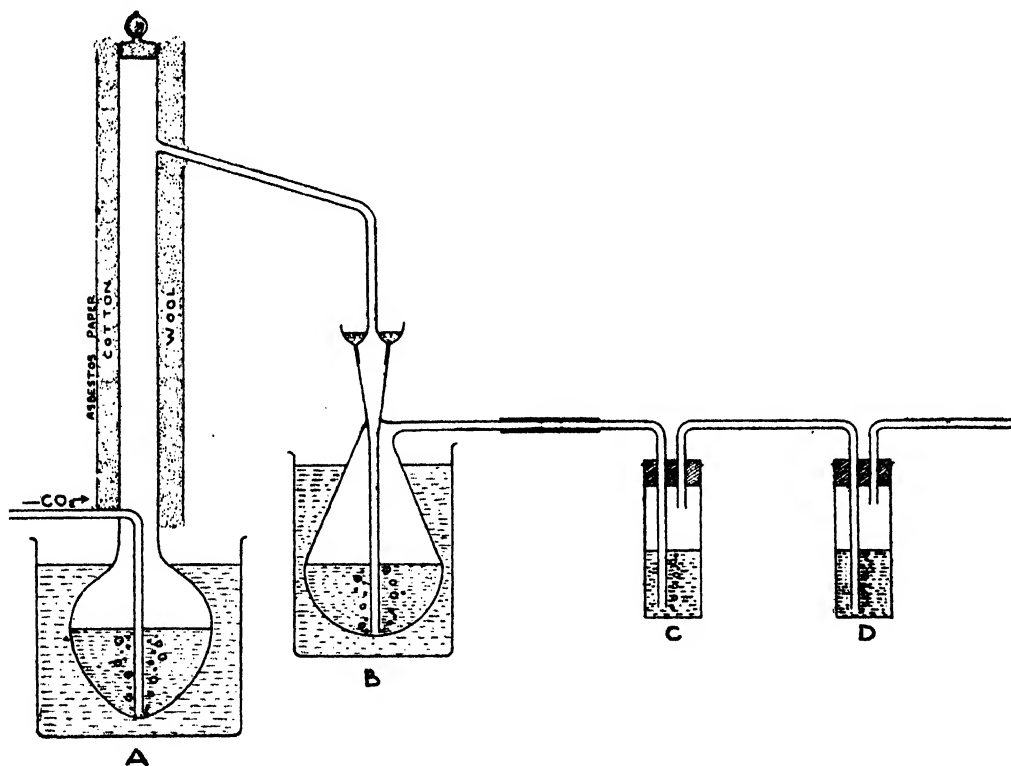
It was also necessary to study the action of hydriodic acid on substances containing the methylene-oxy group which is contained in apiol and related bodies, apart from the action on methoxyl groups. For this purpose piperonal



was chosen, and treated with hydriodic acid under the conditions given in the experimental portion. No iodine compound of sufficient volatility under the conditions of the experiment passed into the absorption tubes, which was rather surprising in view of the possibility of methylene iodide being formed and passing over. This was also confirmed by the action of hydriodic acid on Merck's pure

crystallised apiol, which gave a yield somewhat less than that calculated from two methoxyl groups, no volatile compound having come from the methylene-oxy group.

METHOD USED IN DETERMINING RELATIVE METHOXYL GROUPS.—The apparatus used was a modification of the usual Zeisel apparatus designed by L. V. D. Scorah, M.Sc., A.I.C., for use in the determination of glycerin, and described now with his kind permission. It has the advantage of employing ground glass joints in all places where iodine, hydriodic acid or organic iodine compounds may come in contact with the joint. Carbon dioxide is used to sweep along the products of decomposition into the absorption tubes, and the bulbs are blown in such a way as to ensure the maximum of disturbance consistent with slow gas-bubbling.



The oil under examination was weighed in suitable quantity into an open glass capsule, and lowered by means of a wire into the bulb A; 20 ml. of 57 per cent. (by weight) hydriodic acid, of constant boiling point, were then added, and a slow stream of carbon dioxide, purified by bubbling through a wash-bottle containing sodium carbonate solution, was passed through the apparatus. The rate of flow was regulated to about three to five bubbles per second. Tubes C and D contained a few ml. of 10 per cent. alcoholic silver nitrate solution. The bulb A was surrounded by a glycerin bath and heated to 140° C. during the experiment. The

bulb B contained red phosphorus suspended in water and was surrounded by a water-bath kept at 70° C. The reaction was usually complete in about 60 minutes, as was shown by the absence of precipitate in a fresh tube of silver nitrate replacing those taken away at C and D after this time had elapsed. After evaporation of the alcohol, boiling water and a little dilute nitric acid were added, and the silver iodide filtered and washed on a Gooch crucible in the usual way. A blank always preceded a series of experiments and did not exceed a mgrm. or so of silver iodide.

RESULTS WITH COMMERCIAL APIOLS.—Several commercial apiols from different sources were tested under the above conditions, and the results are embodied in the table which follows. The piperonal and pure triolein, referred to above, were also treated under the same conditions.

Origin.	Character.	Sp. Gr. 15°/15°C.	Refract. Index. n_D^{20}	Rota- tion 20°C.	Saponi- fication value.	Zeisel value expressed as wt. of (CH ₃ O) from 1 grm. of material.	Colour on Lovibond's tintometer scale at dilution of 1:7,500, in $\frac{1}{2}$ inch cell.			
							Read immediately.		Read after 20 hours.	
							Red.	Yellow.	Red.	Yellow.
German "Merck's white crystal- line"	White crystals m.pt. about 30° C.	1.175	1.5370	— 0° 6'	7.7	0.2582	7	5	Unreadable	
French "apio- line"	Slightly yellow liquid: no crystals on standing	1.133	1.5328	—	7.0	0.2675	4	8	12	10
French "apiol"	Thick green oil	0.9729	1.4840	—	175	0.0256	0.4	0.4	0.7	1.0
English "apiol"	Green oil: no crys- tals on standing	1.0606	1.5080	—	67.0	0.2386	2.0	9.5	5.0	13
„ „	Thick green oil depositing crys- tals on standing	1.036	1.5005	—	117.7	0.1190	3.0	4.5	3.0	9
German "Parsley seed oil"	Slightly yellow: liquid no crystals on standing	1.0713	1.5260	— 7° 0'	8.0	0.0712	11	9.6	Unreadable	
Unknown	Green oil	1.012	1.4989	—	—	0.0781	Not available			

CONCLUSIONS.—Merck's specimen was not quite pure, as shown by lack of sharpness in melting point, slight optical activity and saponification value. The Zeisel value was somewhat below that demanded by theory, though it is possible that a 100 per cent. yield of silver iodide is not realisable. The French "apioline" gave an almost theoretical result for the Zeisel value of pure apiol, though this was probably fortuitous, since myristicin and tetramethoxyl allyl benzene might, in suitable proportion, give this Zeisel result and were both probably present. The so-called French "apiol" obviously contained little or no methoxyl constituent, being, in fact, an almost pure glyceride. Triolein gave a Zeisel value only slightly below this specimen, although the colour test carried out according to the B.P.

Codex was satisfactory. The tintometer test at great dilution indicated almost total lack of specific colour-producing substance, showing how misleading the old colour tests may be. The high viscosity and ready solubility in 90 per cent. alcohol of the French "apiol" indicated gross adulteration with castor oil.

The first of the English apiols contained probably one-third of its weight of glyceride, judging from its saponification value. The Zeisel value was higher than would be accounted for by assuming the remaining two-thirds to be pure apiol, indicating the presence of a tri- or tetra-methoxy compound.

The second of the English apiols contained more than one-half of its weight of glyceride. The Zeisel value bore approximately the same relation to the non-glyceride portion as was found in Merck's pure apiol or the French "apioline."

The last two specimens were distinctly low in methoxyl content, and the low saponification value points to their being distilled rather than extracted oils. The German parsley seed oil gave a very high colour figure, showing little agreement with the methoxyl content. The colour was actually a good deal higher than Merck's specimen, whereas the Zeisel value was less than one-third. In view of this, it is evident that the colour test with sulphuric acid, particularly at low dilutions, does not have the value usually ascribed to it.

SUMMARY.—The methods hitherto employed in the examination of apiol have been applied to certain commercial samples.

An improved method of carrying out the sulphuric acid test, employing the Lovibond tintometer, has been described. It has been concluded that the methoxyl content, determined by a modified Zeisel process, is the most distinguishing criterion, in conjunction with various physical data.

I wish to thank the Government Chemist for permission to publish this work.

GOVERNMENT LABORATORY,
CLEMENT'S INN PASSAGE, W.C.

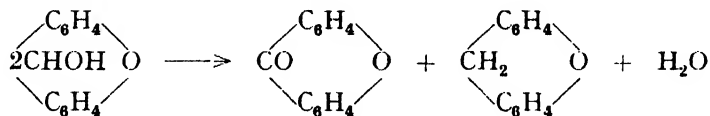
The Preparation and Properties of Xanthidrol as a Reagent for Urea.

By F. G. KNY-JONES, B.Sc. AND A. M. WARD, B.Sc., Ph.D., A.I.C.

XANTHYDROL is a sensitive reagent for the detection and determination of urea (see R. Fosse, "L'uree. (*Recherches de chimie analytique, biologique et agricole.*) Les fonctions dixanthopyranol, xanthidrol et sel de pyryle." Paris, 1928). It is, however, so unstable that alleged specimens are often only the decomposition products (xanthone and xanthane), which do not give condensation products with urea. Commercial specimens of xanthidrol accordingly may fail to detect the presence of urea.

Xanthidrol was prepared by reducing xanthone, the latter being readily obtained by distilling salol, as described in *Organic Syntheses* (Vol. VII, p. 84). The product, consisting of pale yellow needles, was extracted under a reflux condenser with small quantities of acetone until the extracts, which were at first yellow, became colourless. The solid remaining was then dissolved in acetone (moderately soluble in the hot solvent), giving a colourless solution, from which xanthone crystallised in colourless needles, m.pt. 174° (uncorr.). A further quantity of pure xanthone may be obtained from the various liquors. Xanthone has previously been prepared colourless by Dhar (*J. Chem. Soc.*, 1916, 109, 745) by repeated crystallisation from acetic acid or nitrobenzene.

The reduction of an alcoholic suspension of xanthone was carried out by means of sodium amalgam (*Organic Syntheses*, Vol. VII, p. 88; Fosse, *op. cit.*, p. 287), and this method appears to be entirely satisfactory. Drying the product at 40–50°, however, as described in *Organic Syntheses*, usually resulted in complete decomposition, mainly to xanthone and xanthane:



together, possibly, with some dixanthidryl ether. Xanthidrol was accordingly filtered off from the suspension obtained by pouring the alcoholic solution into water. (The aqueous filtrate from the xanthidrol always became turbid after acidifying, and the white emulsion, which slowly turned pink, solidified on standing. *o*-Phenoxybenzoic acid, m.pt. 113°; mol. equivalent, by analysis of silver salt, 216; calc., 212, was obtained from this.) The xanthidrol was rapidly dried on a porous saucer at room temperature, and at once used, or else kept dissolved in ethyl alcohol until required. It was frequently found that a specimen of xanthidrol, dried at room temperature, had undergone almost complete decomposition at this temperature after a few days. The alcoholic solution is much less prone to decomposition, and such a solution after keeping for 3 months still gave a

copious precipitate with an aqueous solution of urea and glacial acetic acid (compare Fosse, *op. cit.*, p. 10).

The melting point of 120–123° C. for xanthyrol, given in *Organic Syntheses*, was sometimes observed, but the m.pt. is dependent upon the conditions of heating, since xanthyrol decomposes above its m.pt., mainly into dixanthyryl ether (m.pt. about 200°, Meyer and Saul, *Ber.*, 1893, 26, 1276). No mention is made in *Organic Syntheses* of this decomposition, but it is quite definite. Thus the temperature of a specimen of xanthyrol in a capillary tube was slowly raised from room temperature; melting began at 117° C., and was practically complete at 123° C.; bubbles then rose through the liquid (135–140° C.), and the material began to resolidify at 140° C. The colourless solid again softened at about 160° C., the main melting was above 190° C., and the temperature reached 201° C. before all had melted. A separate sample, plunged in the bath at 135° C., melted completely, decomposed, and re-solidified. Melting again commenced at about 190° C., and was complete at 198° C. Different experiments gave varying temperatures for these phenomena, but the general behaviour was in all cases as given above. Melting-point determinations of this compound, therefore, afford little criterion of purity, and the homogeneity of the product was checked by the condensation of its alcoholic solution with aqueous urea in the presence of glacial acetic acid, as described by Fosse; if the solution, after separation of the condensation product, gave no precipitate or only a slight turbidity on pouring into water, the initial material was judged to be xanthyrol only. (In some experiments, a small precipitate was thrown down on pouring the solution into water, but this was found to be the urea condensation product.)

In using xanthyrol for the detection or determination of urea, it therefore seems best to prepare this substance immediately before it is required by reducing xanthone, which is quite stable, by means of alcoholic sodium amalgam. The alkaline alcoholic solution is poured into excess of water, the product filtered off, washed, partly dried at room temperature, and re-dissolved in alcohol. A methyl or ethyl alcoholic solution of xanthyrol appears to be much more stable than the solid; it seems useless to attempt to keep the solid, even at room temperature, under ordinary conditions for any length of time.

One of us (A.M.W.) is indebted to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the cost of the materials.

SIR JOHN CASS TECHNICAL INSTITUTE,
LONDON, E.C.3.

Electrometric Determination of Copper.

II. APPLICATION OF VOLHARD'S METHOD TO ELECTROMETRIC ANALYSIS.

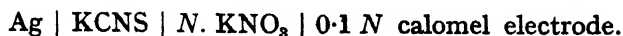
BY MARJORIE E. PRING, M.Sc., AND
JAMES F. SPENCER, D.Sc., Ph.D., F.I.C.

IN 1878 Volhard described a method for the volumetric determination of copper (*Annalen*, 1878, **190**, 1). In this method the solution of a copper salt, after being made neutral, was saturated with sulphur dioxide, raised to the boiling point and treated with a measured excess of a standard solution of potassium thiocyanate. When cold, the solution was filtered from the precipitated cuprous thiocyanate and an aliquot portion of the filtrate titrated with standard silver nitrate solution, using a nitric acid solution of a ferric salt as indicator.

Since it has been shown by Behrend (*Z. physikal Chem.*, 1893, **11**, 476) that a solution of thiocyanate may be titrated electrometrically by silver nitrate, using a silver electrode coupled with a calomel half-cell, it appeared possible that the methods of electrometric titration could be applied to Volhard's process. Further consideration indicates that the process may be simplified. It is obvious that, in the method as originally put forward, the cuprous thiocyanate must be removed before titration with silver nitrate.

Before proceeding to examine the titration of copper salts it was necessary to ascertain that the sulphur dioxide can be entirely removed from the solution by a moderate amount of boiling, for should any remain in the solution, since it is neutral, silver sulphite would be precipitated. To settle this point, a solution of potassium thiocyanate was titrated with silver nitrate and a similar solution was saturated with sulphur dioxide, boiled until the odour of the gas had disappeared, cooled and titrated electrometrically.

The titration was carried out as described previously (*ANALYST*, 1929, 509), using a silver plate and a 0.1 N calomel electrode. Since silver salts are being used, it is necessary to interpose a "salt bridge" between the titration vessel and the calomel electrode. The cell actually measured is represented by the scheme:



The results of the two titrations are given in the table.

Titration of 10 c.c. 0.1 <i>N</i> KCNS + 100 c.c. H ₂ O untreated with SO ₂ .		Titration of 10 c.c. 0.1 <i>N</i> KCNS + 100 c.c. H ₂ O after treatment with SO ₂ .	
0.1 <i>N</i> AgNO ₃ added. c.c.	Voltage.	0.1 <i>N</i> AgNO ₃ added. c.c.	Voltage.
1.42	+0.014	0.00	+0.051
3.00	+0.008	1.31	+0.030
4.52	+0.005	2.82	+0.021
5.90	±0.000	6.20	+0.014
6.94	-0.006	7.05	+0.001
7.96	-0.011	9.05	-0.025
8.87	-0.028	9.16	-0.030
9.04	-0.032	9.28	-0.040
9.20	-0.038	9.33	-0.049
9.34	-0.051	9.38	-0.055
9.42	-0.060	9.43	-0.067
9.46	-0.082	9.48	-0.089
9.53	-0.132	9.53	-0.121
9.57	-0.138	9.62	-0.123
9.73	-0.143	9.76	-0.128
10.05	-0.161	9.86	-0.133

End-point 9.50 c.c.

End-point 9.50

These figures, as will be shown later, prove that the sulphur dioxide can be removed from the solution without undue boiling and that the change of E.M.F. at the end of the titration is sufficiently great to make the end-point easy of determination.

TITRATION OF SOLUTIONS OF COPPER SALTS.—Ten c.c. of a 0.2 *N* solution of copper sulphate were saturated with sulphur dioxide, 20 c.c. of 0.1 *N* potassium thiocyanate solution were added, and the solution boiled until the sulphur dioxide had been expelled. The precipitated cuprous thiocyanate was white. Water (150 c.c.) was added, and the solution left until cold. A silver plate and a 0.1 *N* calomel electrode were inserted, the latter through a potassium nitrate bridge, and the excess of thiocyanate was titrated with 0.1 *N* silver nitrate. The E.M.F. of the titration cell was read after each addition of silver nitrate, and the quantity of silver nitrate was plotted against the voltage, and a titration curve drawn. An example of such a curve is shown in Fig. 1, from which it can be seen that the E.M.F. falls rapidly at the commencement of the titration; it then remains almost stationary until within a few cubic centimetres of the end-point, when it falls rapidly. The end-point is fairly well marked, but it may be found more exactly by plotting the rate of change of E.M.F. with changing amount of silver nitrate, $\frac{\Delta E}{\Delta c}$, against the volume of silver nitrate added, as shown in Fig. 2. The end-point can be made sharper if no water is added other than that necessary to rinse the tube by which the sulphur dioxide is led into the solution. The type of curve

obtained in such circumstances is seen in Fig. 3, in which the change of E.M.F. at the end-point is well marked, and from which the titre can be read directly.

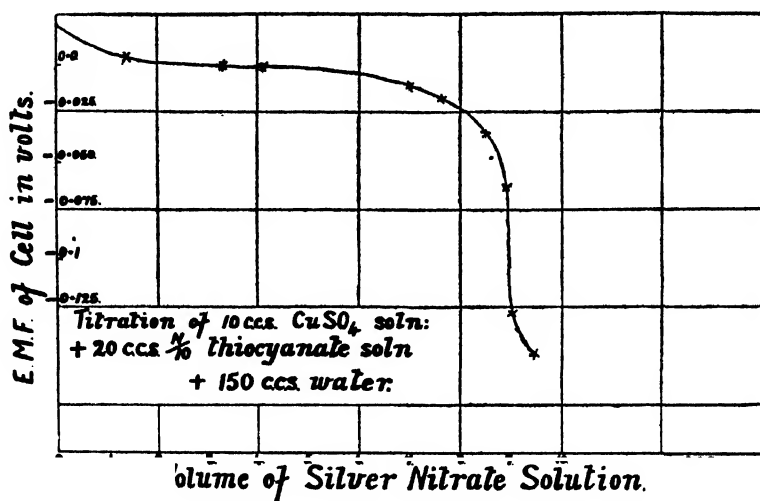


Fig. 1.

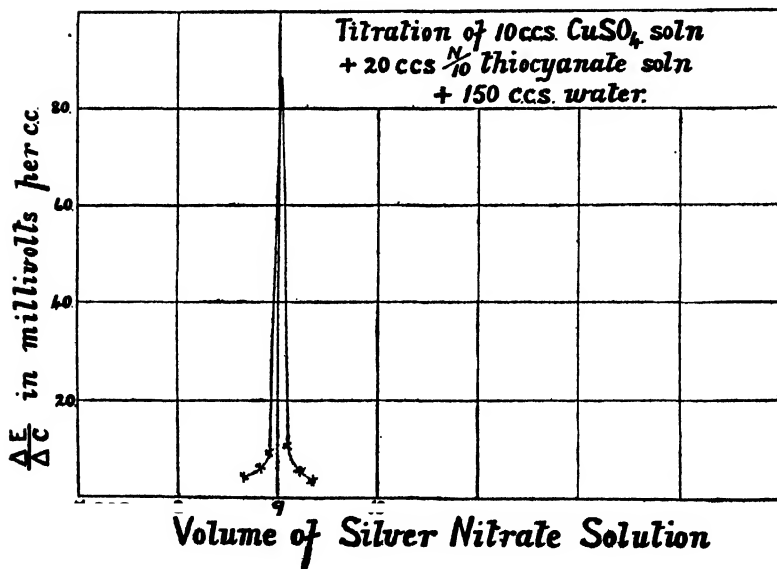


Fig. 2.

To obtain such a sharp end-point it is necessary that the titration should be finished slowly, for the E.M.F. takes a little time to become steady as completion is approached.

EFFECT OF DILUTION OF THE COPPER SOLUTION.—The previous experiments have shown that the end-point of the titration becomes less sharp the more dilute the copper solution. Therefore to ascertain the limit of dilution permissible for accurate determination, solutions of 0.04 *N* and 0.02 *N* were treated with excess of 0.02 *N* and 0.01 *N* potassium thiocyanate solution, respectively, and the excess

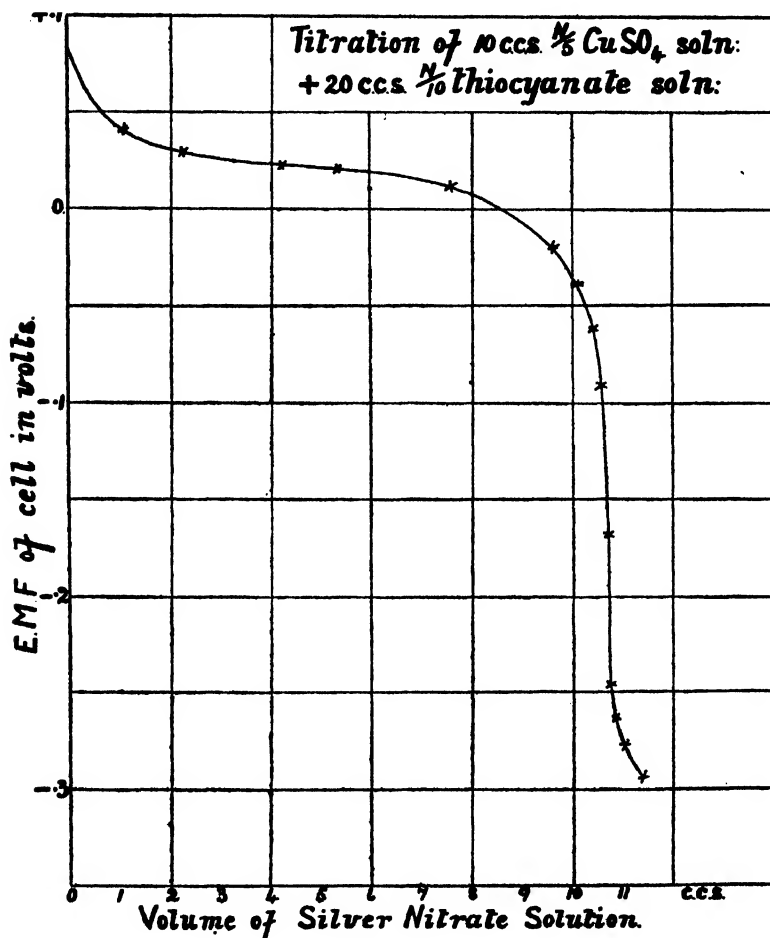


Fig. 3.

titrated with an equivalent solution of silver nitrate. The end-point was much less sharp with the more dilute solution. In the case of the 0.04 *N* solution the change of E.M.F. is not very marked at the end-point, but it is sufficient (Fig. 4) to allow the titration being carried out, whilst with the 0.02 *N* solution the end-point could not be deduced from the titration curve. Consequently, to obtain a satisfactory end-point, the copper solution must have a concentration greater than 0.04 *N*, and it must not be diluted other than by the reagents.

ACCURACY OF THE METHOD.—To define the accuracy of the method, several series of titrations were carried out with carefully standardised solutions of copper sulphate. The solutions were prepared from accurately weighed quantities of pure material, and the concentration of the solution was checked by electrolysis. Silver nitrate solutions were made from the pure salt and checked by titration with standard sodium chloride. The solutions of potassium thiocyanate were standardised by means of silver nitrate solutions and the titration was carried out as described above. The table gives the data of a series of measurements.

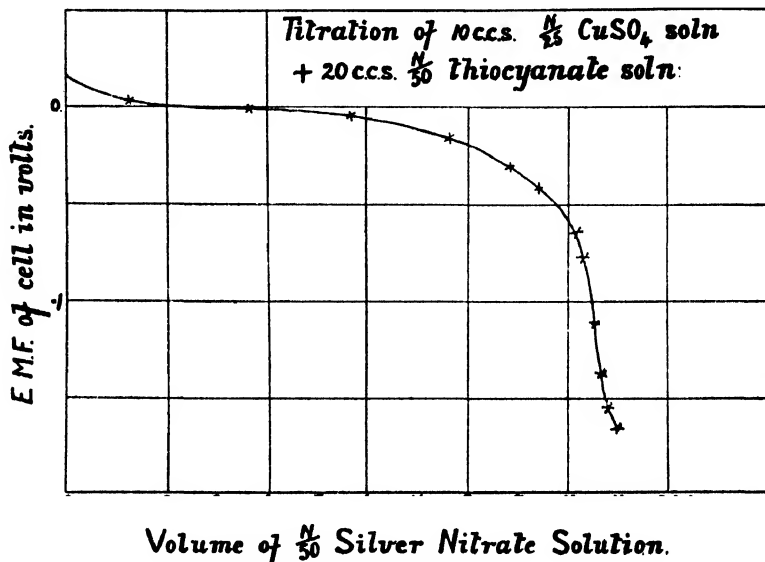


Fig. 4.

10.06 c.c. CuSO_4 0.2002 N + 20 c.c. KCNS 0.09634 N + 100 c.c. H_2O titrated with 0.1027 N AgNO_3 .

AgNO_3 c.c.	Voltage.	AgNO_3 c.c.	Voltage.	AgNO_3 c.c.	Voltage.	AgNO_3 c.c.	Voltage.
5.99	+0.018	6.17	-0.025	6.01	-0.010	5.90	+0.011
6.90	0.021	7.22	-0.006	6.95	± 0.000	7.03	0.015
7.97	0.039	8.05	+0.002	7.90	+0.005	7.91	0.021
8.20	0.042	8.34	0.013	8.19	0.021	8.20	0.025
8.48	0.051	8.61	0.030	8.43	0.030	8.50	0.032
8.60	0.058	8.71	0.039	8.66	0.040	8.71	0.050
8.70	0.062	8.81	0.052	8.78	0.052	8.81	0.064
8.80	0.072	8.86	0.061	8.90	0.075	8.88	0.079
8.90	0.090	8.91	0.080	8.95	0.090	8.93	0.102
8.96	0.130	8.97	0.113	9.00	0.130	8.98	0.127
9.00	0.141	9.03	0.125	9.05	0.149	9.04	0.132
9.11	0.146	9.10	0.130				

End-point 8.94

End-point 8.94

End-point 8.96

End-point 8.94

The average titre of the copper sulphate solution from the values above is 8.95 c.c., whilst the calculated titre has the same value.

In a further series of titrations 9.97 c.c. of CuSO_4 0.03995 *N* were treated with 19.96 c.c. of KCNS, 0.1038 *N*, and the excess thiocyanate titrated with AgNO_3 0.09856 *N*. In four successive experiments the volume of silver nitrate required was 10.89, 10.91, 10.91 and 10.90 c.c., respectively. This gives an average titre of 10.90 c.c., whilst the calculated value is 10.91 c.c. From the foregoing results it is clear that the agreement between the calculated titre and the experimental value is very close, both for 0.2 *N* and 0.04 *N* solutions of copper sulphate. It has already been shown that solutions more dilute than 0.04 *N* do not yield a satisfactory end-point.

INFLUENCE OF ZINC AND IRON ON THE ACCURACY OF THE METHOD.—In the course of analysis of copper-containing materials, iron and zinc are frequently found, and in such cases it would be very convenient if the copper could be determined in the presence of these metals. Consequently it was decided to ascertain whether the presence of iron and zinc has any effect on the accuracy of the method described. A solution of copper sulphate of approximately 0.2 *N* was diluted with an equal volume of water, 0.1 *N* zinc sulphate, and 0.1 *N* ferric alum, respectively; 10 c.c. of each of the mixtures were treated as described above, and the excess of thiocyanate titrated with silver nitrate. The results are given in the table below for a series of four titrations in each case.

Volume of AgNO_3 solution required.		
CuSO_4 alone. c.c.	$\text{CuSO}_4 + \text{ZnSO}_4$. c.c.	$\text{CuSO}_4 + \text{Fe}_2(\text{SO}_4)_3$. c.c.
10.72	10.73	10.72
10.71	10.72	10.70
10.74	10.73	10.69
10.71	10.73	10.73
Mean 10.72	Mean 10.73	Mean 10.71

From these figures it is clear that the divergence from the value obtained with solutions of copper sulphate alone is 0.01 c.c., or less than 0.1 per cent., indicating that the method described is accurate in the presence of either iron or zinc.

CONCLUSION.—Copper may be determined electrometrically in neutral solutions of concentrations down to 0.04 *N*, *i.e.* 1.25 grms. of copper per litre, by saturating the solution with sulphur dioxide, then precipitating cuprous thiocyanate with a measured excess of standard potassium thiocyanate, boiling the solution and, after cooling, titrating the excess thiocyanate with standard silver nitrate. Since the method does not involve filtration of the cuprous thiocyanate, it is both more rapid and more accurate than titration in the presence of a coloured indicator. The determination may be carried out in the presence of iron or zinc salts without diminution of the accuracy.

Acknowledgment is made of a grant from the Department of Scientific and Industrial Research which enabled one of us (M. E. P.) to take part in this work.

The Determination of Small Amounts of Nickel in Steel.*

By B. JONES, B.Sc., A.I.C.

THE determination of nickel in steel is usually carried out by precipitation with dimethylglyoxime or α -benzildioxime in slightly alkaline solution, and treating the precipitate so obtained gravimetrically or cyanometrically. This is a widely-practised method and is excellent when there is sufficient nickel in the steel to yield a precipitate which may be weighed or titrated with accuracy. When, however, the nickel content is less than 0.06 per cent., tests have shown that it is questionable whether the small amounts of this metal are completely precipitated even after a prolonged stand, and whether the determination of nickel in the precipitate is accurate when working on the usual quantity of material. The following small amounts of nickel were taken, and precipitated with dimethylglyoxime in slightly ammoniacal solution in a volume of 100 c.c., and allowed to stand over-night, they were then filtered through a close pulp filter, the precipitate was not washed, and the filtrates were examined for the presence of nickel by the method described later.

Weight of nickel taken, grm.:—

0.0001 0.0002 0.0003 0.0005 0.00075 0.0010 0.0015 0.0020 0.0025

Percentage of total nickel found in filtrate:—

35.0 7.5 5.0 2.0 2.0 2.25 1.0 0.25 Negligible

Difficulties from the above source may be partly surmounted by working on a large weight of sample in order to obtain a larger precipitate, but in certain circumstances large quantities of material are not always available. It appears to be the general procedure with many chemists to report small amounts of nickel in steel as "traces" when there is just sufficient of the element to give a precipitate, after long standing, with the reagent too small for quantitative measurement. In fact, less than 0.1 per cent. is often registered as "traces." When a definite figure is requested, as in the analyses of standard steels, reports from analysts differ as widely as for any element. Thus nickel figures reported by experienced analysts for British Chemical Standard Steel A2 vary from 0.030 to 0.078 per cent., a difference of 160 per cent. While these small amounts of nickel as yet seem to have no appreciable effect upon the mechanical properties of steel, yet from an analytical standpoint the position seems to be in rather an unsatisfactory state, and there appears to be room for a new method which will give a more quantitative significance to these small amounts. A similar position existed with regard to small amounts of chromium until fairly recent years (Evans, *ANALYST*, 1921, 46, 38, 539).

* Communication from the Research Department, Woolwich.

The method proposed is a colorimetric one, and depends upon the reddish-brown colour given by the action of an oxidant upon the dimethylglyoxime complex of nickel. Mention should be made that Feigl (*Ber.*, 1924, 57, 758) obtained a reddish colour by the use of peroxide of lead as the oxidant, but a disadvantage in the use of the latter is that the application of heat and a filtration are necessary. Rollet (*Compt. rend.*, 1926, 183, 212) suggested the use of bromine to replace the oxidant used by Feigl (*vide supra*), and applied it to the determination of nickel in a variety of substances; he gives no figures, however; his claims regarding the quantitative separation of nickel from other elements have not been confirmed; and he ignores interfering elements. Under the conditions to be described, I have found that the employment of sodium hypochlorite as an oxidant gives very satisfactory results, and lends itself very well to colorimetric comparison with a standard. The method involves the isolation of nickel from large amounts of iron and its alloying elements as potassium nickelo-cyanide in ammoniacal solution, the iron, chromium, manganese, etc., being precipitated as hydroxides. This gives a very clean and quantitative separation of nickel from the main constituents of steel. Where, however, copper and cobalt also occur in more than small amounts, the chemical properties are so closely analogous to nickel that they interfere somewhat with the process, as they also form complex cyanides and modify the colour given by nickel. Fortunately it is rare to find the two metals as constituents of steel, and they can be dealt with as described later. Several well-known methods of separation of nickel from iron, such as the ammonium acetate and the zinc oxide methods, were attempted, but were discarded for various reasons. The filtrate from the precipitated hydroxides is used for colorimetric determination.

METHOD FOR PLAIN CARBON STEELS.—One grm. is dissolved in 10 c.c. of hydrochloric acid, and oxidised with 5 c.c. of nitric acid. The solution is boiled for a few minutes and diluted somewhat with cold distilled water. It is then washed into a 200 c.c. standard measuring flask, diluted ammonia (1 part of 0.88 sp. gr. ammonia to 1 part of water) added from a burette or dropping bottle until a slight precipitate of hydroxide is formed which just fails to redissolve in the ferric chloride. Two c.c. of a 1 per cent. solution of potassium cyanide are now added and the flask well shaken, after which 10 c.c. of 1:1 ammonia are added, and the contents of the flask are made up to the mark with warm water. No allowance is made for the volume of precipitate. The whole is poured back into the original flask to mix the contents thoroughly, the precipitate is allowed to settle a little, and filtered off on a large fluted 41 Whatman filter paper, 100 c.c. of clear filtrate being used for the determination. A further 50 c.c. of filtrate are reserved for qualitative purposes, this being desirable, as, in my experience, all plain steels which are assumed to be almost free from nickel contain quantities far in excess of the amount for which the method was designed. The above method of separating nickel from iron is to be preferred to the one recommended in some text-books, of pouring the acid solution into ammonia containing cyanide, as it permits the nickel to react more readily with the excess of cyanide, and also keeps the quantity of

excess ammonia more under control. A large excess of ammonia should be avoided, as it is apt to interfere with the formation of potassium nickelo-cyanide and has a detrimental effect on the qualitative test. This is carried out as follows:—

APPROXIMATE DETERMINATION OF NICKEL.—The 50 c.c. of filtrate are cooled, transferred to a 100 c.c. Nessler glass, and diluted to the mark with water. Two c.c. of a clear solution of dimethylglyoxime in alcohol (just short of saturation) are added, the contents stirred with a glass rod, 1 c.c. of commercial sodium hypochlorite solution added, and the whole again stirred. The solution, on standing, will develop a reddish-brown colour if nickel is present, and is matched as follows:

Another 100 c.c. Nessler glass of the same size and bore is filled to the mark with water, six drops of 1:1 ammonia added, followed by 2 c.c. of dimethylglyoxime solution; the mixture is stirred, 1 c.c. of sodium hypochlorite added, and the liquid again stirred. Three drops of a standard nickel solution containing 0.00005 gm. per c.c. are run into the standard Nessler glass from a narrow 10 c.c. burette, and mixed. The colours are compared by viewing the glasses vertically over a white tile inclined at an angle to act as a light reflector, and the colour is matched by adding the standard solution, three drops at a time, and stirring after each addition, with intervals of several minutes between additions.

When the colour of the standard approaches that of the assay, additions must be made very cautiously. The colours of the two solutions may not be of exactly the same tint, owing to the interference of ammonium salts and decomposition products from the excess of cyanide added, which impart a brownish tint, but the amount of nickel registered by taking the reading when the intensity of colour of the solution is identical is nevertheless near to the truth.

The tint of the test solution improves on standing, and in some cases the qualitative figure is identical with the one finally obtained, although sometimes higher when the copper content is fairly large, but the interference of copper in the test is almost negligible when present in amounts usually found in steels, as any colour given is discharged by the potassium cyanide present in the filtrate.

Meanwhile, the main 100 c.c. filtrate are made just acid with hydrochloric acid, 5 per cent. of the strong acid is added in excess, and hydrogen sulphide is passed into the warm solution in a rapid stream for 15 minutes. Any copper sulphide (mixed with a little sulphur) is allowed to settle out on the water-bath, and when the precipitate has coagulated it is filtered through a pulp filter into a 600 c.c. wide-mouthed beaker and washed with a dilute solution of an electrolyte, such as 5 per cent. ammonium chloride.

Long standing is not necessary to remove the whole of the copper, as traces not precipitated have no effect on the determination; if it is known that only traces are present, this stage may be omitted. The filtrate is boiled down to low bulk, and then taken from the source of heat, and 50 c.c. of concentrated nitric acid added to destroy ammonium salts. A rather brisk ebullition occurs at this stage, and further heat is applied cautiously, the whole being taken to complete dryness, but

not baked for any length of time; further small additions of nitric acid may be necessary to complete the destruction of the ammonium salts. The residue is taken up with hot water, heated till it is dissolved, filtered, if necessary, and cooled.

COLORIMETRIC DETERMINATION.—It is now ready for colorimetric determination, either on the whole solution, or after being made up to a known volume, and a suitable fraction taken which will be indicated by the qualitative test. If the nickel content is very minute as shown by that test, another determination may be made *de novo*, starting with a 4 grm. sample, making the solution up to 500 c.c., and using half for the determination. A good working idea of the nickel content of the sample is obtained in about 45 minutes from the commencement of the experiment. For colorimetric measurement the solution should not contain more than 0.1 mgrm. of nickel, *i.e.* 2 c.c. of standard solution, or results will tend to be inexact, as it is difficult to determine the changes of tint with more concentrated solutions.

The colour reaction is very sensitive and will detect 0.01 mgrm. in 100 c.c. of solution, or 1 part in 10,000,000. It is a very stable colour, remaining almost of the same intensity till next day, thus ensuring an accurate comparison in a slow titration. There is usually no "blank" due to reagents.

The standard nickel solution in these experiments was made by dissolving 0.05 grm. of Hilger's spectroscopically standardised nickel in dilute nitric acid and making up to one litre.

TEST OF THE PROCESS.—Unsuccessful attempts were made to find a steel free from nickel. The fact that much more nickel is found in steels than in irons, suggests that the source of the nickel is from steel scrap used in the manufacturing process. Armco iron was also quite unsuitable for blank tests; even some electrolytic irons contained as much as 0.01 per cent. of nickel, but some specially deposited iron made in the Research Department, Woolwich, gave only 0.003 per cent., and this was used in the test experiments.

Sample analysed.	Weight taken. Grms.	Burette reading. c.c.	Weight of nickel. Grm.	Nickel. Per Cent.
Electrolytic iron A	4	1.20×2	0.00012	0.003
Electrolytic iron B	4	2.00×2	0.00020	0.005
*Electrolytic iron C	4	1.60×4	0.00032	0.008
*B.C.S. cast iron "B"	4	1.20×4	0.00024	0.006

* Final solutions made up to 200 c.c. and 100 c.c. taken.

Varying amounts of standard nickel solution were added to a solution of electrolytic iron A, and the following results were obtained. The rather large blank was unavoidable.

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Weight of sample. Grms.	Nickel added.		Burette reading. c.c.	Blank on E.1. c.c.	Net burette reading. c.c.	Nickel recovered.	
	Grms.	Per Cent.				Grm.	Per Cent.
4	0.00005	0.0012	1.60	1.20	0.40×2	0.00004	0.001
4	0.00008	0.0020	2.00	1.20	0.80×2	0.00008	0.002
*4	0.00015	0.0037	1.30	0.60	0.70×4	0.00014	0.0035
*4	0.00020	0.0050	1.55	0.60	0.95×4	0.00019	0.0047
*4	0.00028	0.0070	1.90	0.60	1.30×4	0.00026	0.0065
1	0.00005	0.0050	0.80	0.30	0.50×2	0.00005	0.0050
1	0.00010	0.0100	1.30	0.30	1.00×2	0.00010	0.0100
*1	0.00020	0.0200	1.10	0.15	0.95×4	0.00019	0.0190
*1	0.00030	0.0300	1.55	0.15	1.40×4	0.00028	0.0280

* Final solutions made up to 200 c.c. and 100 c.c. taken.

The following plain carbon steels were analysed for nickel by precipitation with dimethylglyoxime on a 5 gram. portion, the precipitate allowed to stand overnight, and then treated cyanometrically. The result was compared with the figure obtained by the method under discussion.

Steel.	Precipitation and titration process.	This process.
	Per Cent.	Per Cent.
1	0.011	0.024
2	0.021	0.030
3	0.023	0.042
4	0.040	0.048
5	0.057	0.060
6	0.070	0.072
7	0.082	0.083
8	0.150	0.153

The above results suggest that there is a solubility effect which comes into play in the precipitation method, which manifests itself rather strongly below a certain value, *i.e.* 0.06 per cent.; this shows that amounts of nickel below this figure require to be determined by another method.

ALLOY STEELS. EFFECT OF ALLOYING ELEMENTS ON THE PROCESS.—Tests were carried out to ascertain the effect of elements alloyed with iron; varying amounts of these elements were added to electrolytic iron A, and the filtrates were examined for the presence of the added elements.

Manganese.—One gram. portions of E.1 were dissolved as described, and amounts of reduced *N*/10 potassium permanganate added, after which the conditions of the process were followed. The filtrates were boiled to a small volume, nitric acid added, and the liquid taken to almost dryness, 30 c.c. of nitric acid (sp. gr. 1.2), added, and the manganese was determined colorimetrically.

N/10 KMnO_4 added. c.c. Grm. of manganese.	N/10 KMnO_4 required.
1 = 0.0011	<1 drop
5 = 0.0055	<1 "
7 = 0.0077	<1 "
10 = 0.0110	1 "
15 = 0.0165	<2 drops
20 = 0.022	2 " = 0.1 c.c. = 0.00011 grm. Mn.
30 = 0.033	4 " = 0.2 c.c. = 0.00022 grm. Mn.
50 = 0.055	2.3 c.c. = 0.0025 grm. Mn.

It appears that, under the conditions described, the determination of nickel may be safely carried out in the presence of manganese up to 2 per cent. without interference. Higher amounts would interfere, owing to the formation of a brown colloidal peroxide with the sodium hypochlorite. High manganese steels are treated as described later.

Chromium, Molybdenum, Aluminium, Vanadium are all removed by ammonia.

Tungsten may be removed in the early stages as tungstic acid, but if the amount is small, filtration is unnecessary, as the tungsten is removed quantitatively in the iron precipitate, and the only way in which it interferes is that any separated tungstic acid somewhat obscures the neutralisation point before the potassium cyanide addition.

Copper and Cobalt, when present, appear to enter the filtrate quantitatively when there is sufficient potassium cyanide added to combine with them. Copper steels require no modification of the method described, the copper being removed with hydrogen sulphide, and no further excess of cyanide is necessary, as there appears to be a preferential formation of the nickelo-cyanide, whatever the copper content. Copper when present as a constituent is detected in the qualitative test by a pink permanganic colour with the reagents, which develops into a reddish-brown, and its presence intensifies the colour given by the nickel. This interference is overcome by the addition of 1 c.c. of the potassium cyanide solution, when the colour given by copper is nullified temporarily and the nickel content may then be judged. Cobalt is revealed in the filtrate by a yellow colour of the cobalti-cyanide.

The following experiment was carried out on 1 grm. portions of electrolytic iron A to which was added 0.0001 grm. of nickel and 0.02 grm. of cobalt; the potassium cyanide additions were varied, and nickel was determined in the filtrates as described for the qualitative test.

Potassium cyanide solution added. c.c.	Nickel recovered.
1	Nil
5	Nil
10	Trace after standing
15	1.7 c.c. = 0.000095 \times 2 = 0.00017 grm

It appears that small amounts of nickel do not enter the filtrate quantitatively in the presence of much cobalt until there is an excess of cyanide added to combine with all the latter element first, after which the whole of the nickel enters the filtrate. The high result above is due to appreciable traces of nickel present in the standard cobalt solution. A blank test on the last experiment (no nickel added) was carried out, when 0.8 c.c. of standard nickel solution was required to match the colour obtained.

∴ 1.7 c.c. — 0.8 c.c. = 0.9 c.c. Net = 0.00009 grm. of nickel.

MODIFICATIONS OF PROCESS IN PRESENCE OF ALLOYING METALS. HIGH MANGANESE STEELS.—The sample is dissolved in 30 c.c. of nitric acid (sp. gr. 1.2), evaporated to a small volume, and 50 c.c. of strong nitric acid added. The solution is cooled, and 5 c.c. of chloric acid added, after which it is boiled for 5 minutes and again cooled; a further 50 c.c. of strong nitric acid and 5 c.c. of chloric acid are added, and the solution is again boiled for 5 minutes. It is then filtered through asbestos, after cooling, a gentle suction being applied, and the precipitate is washed with strong nitric acid. This treatment, which is a modification of the Ford and Williams process, removes manganese as the peroxide, and avoids the addition of potassium salts, an excess of which interferes with the final colour given by nickel. The solution is transferred to a large wide-mouthed beaker and rapidly evaporated to a small volume, after which 10 c.c. of hydrochloric acid are added, and the solution boiled for a few minutes. The solution is now treated in exactly the manner described for plain steel.

COBALT STEELS.—Separation of cobalt from small amounts of nickel by means of α -nitroso- β -naphthol, after heating the filtrate with sulphuric acid until fumes appeared, was attempted, but was abandoned, as it gave low results for nickel. It was then decided to make a direct determination of nickel by keeping the cobalt in solution as the cobalti-cyanide. Sufficient potassium cyanide must be added to combine with all the cobalt and nickel present, and it is essential to know approximately the cobalt content of the steel. Thus for every 0.01 grm. of cobalt present, 5 c.c. extra of 1 per cent. potassium cyanide solution must be added. The yellow colour given by the cobalti-cyanide interferes when the amount of nickel is very low, and allowance must be made for it. This is done in a Walpole colorimeter. (ANALYST, 1925, 50, 391.)

The filtrate is divided into two equal parts, the volume of these being indicated by the approximate test, and made up to 100 c.c., each in Nessler glasses. These two tubes, A and B, are placed in the upper compartment of the colorimeter, and immediately over two other tubes, C and D, respectively, in the lower compartment. The two latter contain six drops of 1:1 ammonia and the reagents, while the reagents are added to A. The contents of the tube D are now titrated with the standard nickel solution until a match is obtained, vertically through A and B. Copper does not interfere in this process, owing to the excess of cyanide in the filtrates which neutralises the effect of any copper, unless this is present in large

amounts, when it must be removed in the initial stages by treatment with hydrogen sulphide after dissolving the sample in hydrochloric acid.

The following results were obtained by adding small amounts of nickel to 1 grm. portions of electrolytic iron A, to which were also added elements as described.

Nickel added.		Metals added.		Nickel recovered (on half quantity).			
Grm.	Per Cent.	Grm.	Per Cent.	Blank. Grm.	Gross. Grm.	Net. Grm.	Per Cent.
0.00005	0.005	Cr 0.20	20	0.000015	0.00004	=0.000025	0.005
0.00010	0.010	{Cr 0.20 Mo 0.01	20 1	0.000015	0.00006	=0.000045	0.009
0.00010	0.010	{Mn 0.20 Cr 0.02	20 2	0.000015	0.000065	=0.00005	0.010
0.00010	0.010	V 0.01	1	0.000015	0.000060	=0.000045	0.009
0.00010	0.010	{Co 0.05 Cr 0.02	5 2	*0.000035	0.000065	=0.000030	0.012
0.00015	0.015	Cu 0.02	2	0.000015	0.000085	=0.00007	0.014
0.00020	0.020	W 0.10	10	0.000015	0.00011	=0.000095	0.019

* Nickel detected in cobalt added; half final solution taken.

Some results are appended which were obtained on various steels, including some British Chemical Standards.

Steel.	Percentage composition.	Results by other processes. Per Cent.	Results by this process. Per Cent.
Q 1	Mn 0.32	0.072	0.074
H R K 34	Mn 1.30	Traces	0.040
S D 2	Mn 1.14, Cr 0.013	Faint trace	0.040
U 2	Mn 0.32, Cr 0.09, W 6.15	0.140	0.144
Z S F C 2	Mn 0.76	0.062	0.065
Armco iron		0.058	0.060
B.C.S. cast iron "B"	Mn 0.63, C 3.06	Not reported	0.006
B.C.S. "P"	Mn 0.706	Traces	0.021
B.C.S. "V"	Mn 0.54, Cr 0.86, V 0.273	Traces	0.024
B.C.S. "H1"	Mn 0.66	<0.03 approx.	0.040
B.C.S. "R"	Mn 0.914, Cu 0.02	None detected by qualitative tests	0.048
B.C.S. "A2"	Mn 0.04, Cr 0.01, Cu 0.067	0.059	0.074
B.C.S. "O1"	Mn 0.617, Cr 0.017, Cu 0.037	0.162	0.153
Stainless steel H Z A	Mn 0.32, Cr 13.5, Si 1.0	0.24	0.22

It will be noted that this table supports the contention that the old methods fail below approximately 0.06 per cent. of nickel.

Notes.

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

THE ACTION OF AIR ON FLOWERS OF SULPHUR AND GROUND SULPHUR.

THE following investigation was carried out to determine the action of air on flowers of sulphur and ground sulphur at various temperatures.

The method employed consisted in passing a known volume of air over the sulphur, which was maintained at a constant temperature, and then passing the air through a standard solution of iodine.

The results obtained are shown in Tables I and II.

TABLE I.

Class of sulphur.	Weight of sulphur taken. Grm.	Temperature.	Vol. of air. Cb.ft.	N/100 iodine. c.c.	Equivalent to SO ₂ on weight of sulphur taken. Per Cent.
Flowers	1	17° C.	1	0.1	0.0032
Flowers	1	25° C.	1	0.2	0.0064
Flowers	1	30° C.	1	0.4	0.0128
Flowers	1	40° C.	1	0.5	0.0160
Flowers	1	50° C.	1	0.7	0.0224
Flowers	1	60° C.	1	0.9	0.0288
Flowers	1	70° C.	1	0.9	0.0288
Flowers	1	80° C.	1	1.1	0.0352
Flowers	1	90° C.	1	1.2	0.0384
Flowers	1	100° C.	1	1.3	0.0416

TABLE II.

Ground	1	17° C.	1	Nil	Nil
Ground	1	60° C.	1	Nil	Nil
Ground	1	70° C.	1	Nil	Nil
Ground	1	80° C.	1	Nil	Nil
Ground	1	90° C.	1	0.2	0.0064
Ground	1	100° C.	1	1.2	0.0384

The apparatus employed to carry out these determinations consisted of first a potash bulb to free the incoming air from any sulphur compounds, followed, in succession, by a drying tube of calcium chloride, a test tube containing the sulphur, a wash-bottle with a known quantity of standard iodine solution, a further wash-bottle with a known quantity of sodium thiosulphate solution, and finally a meter for measuring the volume of air passed over the sulphur.

The introduction of the sodium thiosulphate was found, during the preliminary experiments, to be necessary, as an appreciable quantity of iodine is carried over by the air.

The sulphur in the test tube was covered with a layer of cotton wool to prevent any particles of sulphur passing over in the current of air.

The indicated temperatures were maintained by means of a water-bath, throughout the period of each determination, *viz.* $3\frac{1}{2}$ hrs.

It is apparent from the figures in the above tables that:

- (1) Air has little or no action on ground sulphur at temperatures below 90° C.
- (2) Appreciable and increasing quantities of sulphur compounds are evolved from flowers of sulphur in the presence of air at temperatures from 17° C. upwards.

The ground sulphur was sufficiently fine to pass through a 100-mesh sieve to the extent of 99.45 per cent. While it is admittedly a comparatively coarse product, this does not explain the apparent inactivity of the ground sulphur at temperatures below 90° C., whilst the flowers of sulphur shows a steady and progressive increase in the amount of sulphur compounds evolved as the temperature rises.

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Notes from the Reports of Public Analysts.

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY AND COUNTY OF BRISTOL.

REPORT OF THE PUBLIC ANALYST FOR THE YEAR 1928.

THE total number of samples examined was 1400 (805 formal), of which 87 were adulterated, bringing the adulteration percentage to 6.21 per cent., the highest since 1919. The increase in milk adulteration (72 of 747 samples) was responsible for the high general adulteration rate.

A sample of skim milk was not only adulterated with 16 per cent. of added water, but also contained formaldehyde (0.002 per cent.), which was also present in one sample of milk (0.01 per cent.).

UNFERMENTED CORDIALS.—Eleven samples of unfermented cordials, sold as “non-alcoholic British wine,” were examined. These had the following composition:

UNFERMENTED CORDIALS.

Description.	Cider-snap.	Raisin.	Ginger.	Cowslip.	Orange.	Ginger (Brandy).
Sp. Gr.	1041.2	1093.4	1110.0	1112.8	1133.3	—
Alcohol by wt., per cent.	0.68	0.42	0.74	0	0.37	0.10
Alcohol by vol. „	0.87	0.53	0.94	0	0.47	0.12
Proof spirit, „	1.49	0.93	1.62	0	0.76	0.22
Total solids, „	11.27	24.0	26.8	24.4	34.9	48.0
Ash, „	0.15	0.026	0.075	0.066	0.050	.14

UNFERMENTED CORDIALS—*continued.*

Description.	Raisin.	Ginger (Brandy).	Ginger.	Raisin.	Orange.
Sp. Gr.	1097·1	—	1102·9	1108·5	1087·5
Alcohol by wt., per cent.	0·54	0	0·30	0·47	0·23
Alcohol by vol. ..	0·80	0	0·49	0·60	0·29
Proof spirit, ..	1·39	0	0·86	1·05	0·51
Total solids, ..	25·92	51·9	26·20	26·26	22·62
Ash, ..	0·06	0·102	0·095	0·07	0·03

BACTERIOLOGY.—During the year 12,317 specimens were examined.

Examination for Diphtheria.—Westbrook's system of classification was adopted. In this system the Klebs-Löffler and Hoffman organisms are dealt with together as *B. diphtheria* of varying forms, beaded, barred and solid types, in degree of virulence in the above order.

The system, however, was modified to this extent, that when slides afforded evidence of complete characterisation, such slides were further specified by the designating letters KL accompanying the old classification; other slides classified as B (a mixed infection) were regarded as suspicious, while those in which Hoffman forms alone occurred were left in Class C.

The following table expresses the results obtained by this modified system, the classes (A and B) KL, B, C representing the presence and extent of the above organisms, with the specimens submitted by the general medical practitioners of that City:

Class (A & B) KL ..	341	10·41 per cent.
Class B	72	2·20 " "
Class C	535	16·34 " "
Negative	2,327	71·05 " "
Total ..	3,275	100·0 " "

There were thus among these, 10·41 per cent. of cases of undoubted diphtheria discovered, and 2·20 per cent. suspicious cases.

Milk.—Of the 122 samples of graded milk examined, 3 of certified milk, 16 of Grade A milk and 5 of Pasteurised Milk did not comply with the Milk (Special Designations) Order, 1923. Of 16 samples of vended milk, 1 was placed in category 1, and 4 in category 2, the remainder falling below the standard of graded milk.

Raisins.—These were alleged to have been damaged by sea-water or sewage. A portion was macerated in sterile water and inoculations made into MacConkey tubes (glucose). No indication of the presence of *B. coli* was obtained, and there was thus no evidence of sewage.

EDWARD RUSSELL.

GIBRALTAR.

REPORT OF THE CITY ANALYST AND BACTERIOLOGIST FOR THE YEAR 1928.

THE total number of samples and specimens examined was 4020. There was a marked decline (857) in the number of diphtheria swabs examined, but, apart from this, there was an increase in the other branches of laboratory work. Of the 178 samples of food and drugs examined, 31 (17·4 per cent.) were below the standards set out in the Public Health Ordinance.

GOATS' MILK.—The average composition of the samples of goats' milk was:—Fat, 4·16; non-fatty solids, 9·01 per cent. These figures were well above the statutory limits for Gibraltar, namely, 3·5 per cent. of fat and 8·0 per cent. of solids-not-fat.

GOATS' UNBOILED MILK.—To prevent the introduction of milk-borne diseases from Spain all milk must be boiled before being sold in Gibraltar, and the magistrates deal severely with the offence of selling unboiled milk. Among last year's samples two were found not to have been boiled, and a third sample showed contamination with unboiled milk to the extent of about 5 per cent. In one of these cases a fine of £3 with £1 3s. 0d. costs was imposed.

GOATS' MILK—SKIMMED.—Of the 67 samples of goats' milk examined, no less than 24 were deficient in fat. When samples are taken by the inspectors, it is the general rule for vendors to declare that the milk has been skimmed. By so doing they evade the law, for in a test case brought before the High Courts a few years ago the vendor was successful. Experiments made by me have shown that the fat which rises to the surface of hot milk can easily be worked back into the milk again when cold, and there will then be very little difference, if any, in the fat and non-fatty solid contents. In view of the large increase in this malpractice of skimming in recent years, it was thought desirable that amendments to the existing ordinance should be framed to protect the public (*cf.* ANALYST, 1929, 104).

METALLIC CONTAMINATION OF AERATED WATERS.—A systematic examination of the products of the six aerated water businesses in Gibraltar was made during the latter part of the year. While some were free, or nearly so, from metallic impurities, others contained appreciable and even dangerous amounts of lead (*e.g.* up to 0·5 grain per gallon). The origin of the lead in two of the factories was traced to the use of lead piping to connect the carbonator with the bottle-filling apparatus. In another factory lead was getting into the soda water from the solder on the mixer. These sources of contamination have now been eliminated.

A. G. HOLBOROW.

Legal Notes.

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

SAMPLING AFTER DELIVERY.

ON August 12 a wholesale firm was summoned at Ramsgate for giving a false warranty to a grocery firm in respect of a sale of pepper.

The solicitor for the defence asked that the case should be dismissed on the ground that a copy of the analyst's certificate did not accompany the summons, as is required by the Act, but the Bench decided that the case should proceed.

Evidence was then given that the sample had not been taken in the course of delivery, as provided by the Act, but that delivery took place first.

The Bench upheld the objection and dismissed the summons. The Chairman observed that someone was to blame for not sending the analyst's certificate with the summons, and that the inspector should have been instructed to take the sample before delivery of the pepper was complete.

ARTIFICIAL CREAM: AN APPEAL.

ON September 13, the appeal of a "Pure Milk and Cream Company, Ltd." against convictions at Marlborough Street Police Court (see ANALYST, 1929, 542) was heard at London Sessions.

The Chairman, Sir Robert Wallace, announced that the appeal would be allowed on the ground that the proceedings in the Police Court had not been brought by a body entitled to take proceedings under the Act.

Department of Scientific and Industrial Research.

FOOD INVESTIGATION. Report No. 33.

A CRITICAL AND HISTORICAL STUDY OF THE PECTIC SUBSTANCES OF PLANTS.*

A STUDY of the chemistry of the pectic compounds shows that *pectose* is not to be regarded as a substance of invariable composition, but a compound of methoxylated pectin in which from 1 to 8 of the methoxy groups may be replaced by cellulose residues; *pectin* is a neutral methoxy ester of pectic acid containing 11.76 per cent. of methyl alcohol; *pectic acid* is a complex galacturonic acid combined with arabinose and galactose, and between pectin and pectic acid are intermediate forms classed together as pectinic acids. The acid extracted with alkali from beets by Scheibler and Votoček and Šebor is a complex arabic acid of the nature of arabin associated with various carbohydrates, glucose, arabinose and galactose, and is not identical with the metapectic acid similarly obtained by Frémy and others from fruits and other plant tissues. Probably metapectic acid is identical with the *d*-galactose-galacturonic acid, $C_{12}H_{20}O_{12}$, described by Ehrlich as a hydrolytic decomposition product of pectin and pectic acid. Both are amorphous, water-soluble, strongly acid, precipitated by alcohol and mineral acids, form water-soluble calcium and barium salts, and, on oxidation with nitric acid, give mucic acid. The confusion as to the decomposition products is largely explained by the fact that galactose and pentose sugars give rise to furfural on distillation with hydrochloric acid.

EXTRACTION OF PECTIC COMPOUNDS.—The various methods for the extraction of the more important pectic compounds from plant tissues are discussed in detail. A new method for extracting pectose by conversion into pectic acid by hydrochloric acid consists in washing with water to remove the bulk of natural acids and soluble pectic substances, and then boiling under a reflux condenser for successive 3-hour periods with *M*/75 hydrochloric acid. The extract is filtered off, the residue washed with water to free it from the soluble pectic material produced, and the boiling repeated until nothing further is extracted (3 to 5 boilings). If boiled for more than 3 hours, the soluble pectic substances produced tend to decompose or alter physically. Aliquot portions of the total extract, including washings, are hydrolysed with soda and precipitated with acetic acid and calcium chloride, and the total pectic content of the tissues thus found. By deducting the amount of soluble pectin obtained in a separate determination by dissolving out with water and alcohol, the pectose present is found.

* By M. H. Branfoot (M. H. Carré). Obtainable at Adastral House, Kingsway, W.C.2. Price 3s. 6d. net.

On ten 50 grm. samples of fresh, uniform, apple tissue the weight of pectose (as calcium pectate) was between 0.73 and 0.77 grms., averaging 0.75 grm. By staining with ruthenium red, pectic substances not affected by the above treatment were still found present in the middle lamella. By boiling the residue after extraction of pectose, pectin, etc., for successive half-hour periods with dilute sodium hydroxide of concentration not exceeding 0.05 per cent., a gradual solution of cellulose was found to take place, and by solution of their middle lamellae the cells become completely separated. The method affords a relative measure of the extent of the occurrence of pectic constituents in the middle lamella.

Quantitative hydrolysis of pectose into pectin depends on a careful adjustment of temperature, time of action and H-ion concentration of the extracting solution. For the preparation of commercial pectin extracts the raw material should be heated for 5 or 6 1-hour periods at 98° C. with approximately 0.1 per cent. nitric acid. Further purification is effected by filtration through kieselguhr.

PURIFICATION OF PECTIN.—Pectin may be purified by a process of electrolysis. A small parchment dialyser containing distilled water is suspended in a bell-jar containing the pectin solution and having a parchment-covered bottom, which is dipped in a large glass trough of distilled water, with a layer of mercury at the bottom to serve as cathode. Tubes for filling and emptying pass through the cork of the bell-jar, and also a tube filled with mercury in the end of which is fixed a platinum electrode of about 2 square cm., to serve as anode; a reverse current causes precipitation of pectin. The current is kept at 0.25 amp., and the heating effect reduced by placing the electrodes as near together as possible. The water in the dialyser should be changed daily. The average ash content of samples of plant material was thus reduced from 3.1 to 0.5 per cent. in 3 days. Pectic acid of a high degree of purity and of a definite chemical composition may be prepared by Schryver and Haynes's method (ANALYST, 1917, 42, 144).

For the preparation of a clear concentrated and tasteless extract of pectin, on a large scale, Poore's method is satisfactory. The aqueous pectin extract is filtered through kieselguhr, precipitated with 95 per cent. alcohol, and enough absolute alcohol added to the precipitate to convert it into a thick paste. After kneading, the alcohol is removed by pressing. The process is repeated several times at a temperature of 68° C. The purified pectin is then dissolved and concentrated as required.

Pectin may be prepared in powder form by Zoller's method (ANALYST, 1918, 43, 270), whereby purification is effected by precipitation and re-solution, centrifuging, dialysis against running water (but electro-dialysis would be preferable), and evaporation *in vacuo* at a temperature not exceeding 40° C., followed by precipitation by alcohol.

DETERMINATION OF PECTIN.—The determination by precipitation of pectic substances as calcium pectate is discussed by Carré and Haynes (*Biochem. J.*, 1922, 16, 60), and Carré (ANALYST, 1922, 47, 263; *Ann. Bot.*, 1925, 39, 811), and has been found invariably successful by Carré, further confirmation being afforded by Farnell, Hardy and Emmell. The "soluble pectin" of various authors is not necessarily of uniform composition, and the term must be regarded as collective, indicating the mixture of neutral pectin and pectinic acids arising from the various forms of pectose in the tissues.

The relative distribution of the cellulose and pectic material may be ascertained by using Mangin's microchemical methods. By boiling the sections with water for long periods considerable amounts of pectic material are removed from the cell walls, but complete dissociation is not obtained. By boiling with 5 per cent. hydrochloric acid, followed by 2.5 per cent. potassium hydroxide, positive reactions

for cellulose, but negative for pectic compounds are obtained. By treatment with acid alcohol, followed by a solvent for pectic acid such as ammonia, caustic alkali, etc., the pectic compounds modified by the acid are maintained insoluble.

The pectic constituents may be isolated by solution of the cellulose with Schweitzer's reagent.

STAINING METHODS.—Ruthenium red is a valuable stain for the detection of pectic substances if used critically with other stains and combined with chemical methods. The basic stains, such as methylene blue, safranin, etc., do not exhibit specific affinity for pectic substances. Sections are prepared, washed with water, and at once stained in a freshly prepared aqueous solution of ruthenium red (1 part in 5,000 of water). The stain may usually be removed from the non-pectic portions by warming in water. The sections may then be treated on the slide by various reagents effecting decomposition; for example, ammonium oxalate dissolves out all pectic compounds, leaving unaltered cellulose. Hydrochloric acid, followed by potassium hydroxide, may also be used. By such methods the intimate association of the cellulose of the cell walls with pectose was established, and the conception of the middle lamella as a kind of cell cement composed of a complex containing pectic acid or pectates was confirmed.

ENZYMIC DECOMPOSITION.—The distribution of pectic compounds in plant tissues and their possible functions in the plant economy and the changes which the pectic compounds undergo in fruits, especially in the apple, are discussed, together with the enzymes responsible for the pectic changes in certain plant and fruit structures. In the case of pectic decompositions associated with fungal and bacterial diseases a series of pectic changes is effected by enzymes similar to, if not identical with, those normally produced by the plant tissues, and it is probable that the majority of fungal or bacterial secretions contain a mixture of the various enzymes present in normal tissue, *i.e.* pectosase, pectinase and pectase. The secretion of *Rhizopus* (Harter and Weimer), however, probably contained no pectosase. The disintegration of plant tissues produced by fungal diseases, and the similar phenomena accompanying normal death, are regarded as due to a series of pectic changes controlled by enzymes, either present in the living tissues or secreted by the fungi or bacteria.

MANUFACTURE OF FRUIT JELLIES.—In considering the formation of pectin and sugar fruit jellies empirical methods involving concentration by evaporation of unestimated mixtures of the fruit sugar and water are unsatisfactory, because if acid but insufficient pectic materials are present (rhubarb, apricot, strawberry, pineapple, cherry), jelly cannot be produced except by the addition of pectin; or if the fruit contains too little acid (strawberries, cherries, sweet apples, pears, peaches, melons, and figs), prolonged heating merely results in pectic decomposition and caramelisation of the sugar, and acid must be added before jelly is formed (strawberries and cherries are deficient in both pectin and acid). Further, in over-ripe or unsound fruit pectin decomposition has started and increases on heating. A concentration of 0.2 to 1 per cent. of pectin and of acid is regarded as the optimum for jelly production. Pectin is now prepared from many sources, such as sugar-beet residues, and may be added as required. A similar percentage of pectin in different fruits does not necessarily mean similar jellifying powers, and much work has still to be done in this connection. If acid pectin and sugar are present in optimum proportions, 8–10 minutes' rapid boiling produces good jellies. If pectin or acid are deficient, 20 to 30 minutes' boiling will be necessary to bring about concentration by evaporation; but if sugar is deficient, the time will be decreased. More than 30 minutes' boiling is useless, and pectin decomposition takes place, destroying the jellifying power of the mixture. D. G. H.

New South Wales.

ANNUAL REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR 1928.

IN his final report, Dr. Cooksey, the retiring Government Analyst, states that a record number of samples (20,658) was examined during the year, being an increase of 3000 over the previous year. Of these, 15,945 were milks, 2·5 per cent. of which from the metropolitan area were adulterated, and 4·5 per cent. of those from the country districts.

FOOD PRESERVATION BY SULPHUR DIOXIDE ENABLING ACT, 1920.—During the year 1928 this Act was added to the list of legal enactments in force in this State. It was passed and put into operation to legalise the Bullot, or similar processes for the preservation of meat. Under Section 4 of the Act, not only meat, but all foods, are allowed to contain sulphur dioxide (or sulphites calculated as sulphur dioxide) in amount not exceeding 3·5 grains per lb. The second paragraph of this Section provides that "sulphur dioxide" must be applied in the form of a gas by a method approved by the Board of Health, but no restriction is placed on the method, or methods, by which sulphites, which are permitted as an alternative preservative, may be added. The omission, however, is one of considerable importance, since it appears that the Section, as worded, is capable of an interpretation obviously not intended by the framers of the Act, and permits the addition of sulphites to foods up to the limit specified. In connection with the approval by the Board of Health of the method by which sulphur dioxide should be applied, an investigation was carried out in the Chemical Laboratory. (Cf. p. 601.)

A total of 209 samples of raw meat was examined, 136 of which contravened the requirements of the Regulations of the Pure Food Act by containing a preservative. Of 746 raw sausages examined, 222 contained preservative in excess of the amount permitted, while 11 of 150 cooked sausage meats were adulterated by being deficient in meat and by being artificially coloured. Forty-five samples of tripe were found to contain preservative, 22 of which contained sulphites, 5 formalin, 1 nitrite, and 17 boron compounds.

A special examination was made of a number of tripes prepared by a process requiring the use of sodium perborate. This process produces an article clean and attractive in appearance, possessing good keeping qualities. The chemical examination of the final product offered for sale did not show evidence of the presence of a peroxide, but small amounts of boric acid (in the majority of cases, however, less than one-quarter of a grain per lb.) were present.

LIVER EXTRACTS.—Liver extracts having recently been shown to be efficacious in the treatment of pernicious anaemia, a chemical examination of the various commercial preparations on the market was undertaken. Some of these take the form of the dried or desiccated liver substance, whilst others are claimed to be highly active fractions in which the essential principle can be given in concentrated form. The chief disadvantage of the latter type has been its hygroscopic nature, but this is now overcome by packing in sealed glass tubes in dosal quantities.

The composition of the active principle in liver is at present unknown. The analyses, therefore, were not intended as a comparison of the efficacy of the preparations examined, but rather to ascertain as far as possible whether the statements accompanying the articles were correct, and to see that no adulteration was being practised.

Of the two dried liver substances examined, both appeared to be correctly described as having a concentration of four times that of fresh liver, although one sample had considerably more fat than the other.

A good deal of variation in composition, however, is shown in the concentrated fractions ("extracts"), but this may be accounted for by different processes of manufacture. It would appear to be highly desirable to adopt standard methods of manufacture to ensure that liver preparations are of uniform composition, containing the active principle in adequate quantity.

The amounts of copper, iron and zinc were determined in a desiccated substance and in a fractional extract. The other samples analysed were not sufficient in quantity to permit of these determinations being made. From the results obtained in the two samples tested it is inferred that the metallic content bears no relationship to the therapeutic activity.

COMPOSITION OF COMMERCIAL LIVER PREPARATIONS USED IN THE TREATMENT OF PERNICIOUS ANAEMIA.

Sample No.	1.	2.	3.	4.	5.	6.	Average
Country of manufacture	<i>Australia.</i>	<i>England.</i>	<i>U.S.A.</i>	<i>U.S.A.</i>	<i>England.</i>	<i>U.S.A.</i>	composition
Description of sample	Desiccated liver.	Liver extract.	Desiccated liver.	Liver extract.	Liver extract.	Liver extract.	of fresh ox liver.
Weight of substance in container, grms.	114	7.26	28.6	5.88	9.23	2.11	—
Labelled equivalent of fresh liver, grms.	456	226	114	100	226	100	—
Corresponding to:—							
Concentration in comparison with fresh liver	4:1	31:1	4:1	17:1	24.5:1	47:1	—
Water, per cent.	7.80	12.65	7.45	18.60	12.52	9.20	71.2
Ash, "	2.97	21.2	5.35	9.95	11.53	9.94	1.6
Phosphoric anhydride, "	1.58	6.03	2.48	2.62	4.19	5.61	—
Nitrogen, "	9.72	7.52	9.63	7.47	2.92	11.16	—
Protein (N × 6.3), "	61.2	47.4	60.6	47.0	18.4	70.3	20.4
Fat, "	22.7	Nil	8.0	Nil	Nil	Nil	4.5
Carbohydrates (by diff.), "	5.33	18.75	18.6	24.45	57.55	10.56	2.3
<i>Metals (mgrms. per 100 grms.):</i>							
Copper	3.5	—	—	1.8	—	—	—
Iron	22.5	—	—	2.5	—	—	—
Zinc	11.0	—	—	3.1	—	—	—

COD-LIVER OIL TABLETS.—During the year attention was drawn to an American preparation, "Cod-Liver Oil Compound Tablets." Extensive claims in regard to the therapeutic action are made by the manufacturers, cod-liver oil being stated to be "the most active ingredient." It is also claimed that "the extractives used in these tablets contain the entire vitamin content," and "each tablet contains (by extractives) the actual equivalent of a half teaspoonful of cod-liver oil." The chemical test for vitamin A indicated that the quantity present in the tablets examined was not more than would be accounted for by the incorporation of a small amount of cod-liver oil in the pill mass, approximately one-quarter of a grain per tablet. That is to say, it would require 225 tablets to yield the equivalent of a medicinal teaspoonful of cod-liver oil. Biological tests were not carried out in this State, but were made in the laboratories of the Pharmaceutical Society, London, and showed the absence of both vitamins A and D. Stringent regulations are necessary to prevent such gross misrepresentations being made.

TOXICOLOGICAL CASES.—Police and Coroners forwarded exhibits for examination in connection with 68 deaths which formed the subject of inquiry. Among the unusual poisons found in the viscera submitted were arsenate of lead (fruit spray), mercury (a poison which has a very corrosive action on the organs), nicotine, and atropine, the latter derived in the case under notice from liniment of belladonna. In other cases death was found to have been due to strychnine, arsenic, morphine, opium, carbolic acid, formalin (a poison not often used), prussic acid, veronal and cyanide. In 27 cases the analytical examination did not furnish evidence of the presence of poisons. In 4 cases action was taken by the Crown on murder charges, in two of which death was due to slow arsenical poisoning.

In one of these cases, the poison was administered in the form of arsenate of lead (fruit spray), both lead and arsenic being found in the organs.

BLOOD TESTS IN CONNECTION WITH DROWNING.—During the year specimens of blood were forwarded for analysis in connection with deaths supposed to have been due to drowning. It has been found by Gettler (see *U.S. Naval Medical Bulletin*, May, 1922) that in cases of drowning in salt water the blood of the left chamber of the heart contains more sodium chloride than that of the right chamber. In cases of drowning in fresh water the reverse holds, the blood in the left heart containing the lower percentage of sodium chloride. Figures obtained in definite cases of drowning show a difference in the chloride content of the blood of the two chambers of the heart, amounting to at least 19 mgrms. of sodium chloride per 100 grms. of blood.

It is of interest to note that in every case submitted the analytical figures supported the medical diagnosis as to the cause of death, and the method has proved extremely valuable in doubtful cases. The following are the figures obtained in 7 cases examined in the Laboratory:

No.	Sodium chloride. Mgrms. per 100 grms. of blood.		Conclusions drawn from chemical examination.
	Left heart.	Right heart.	
1	566	494	Salt-water drowning.
2	603	603	Death not due to drowning.
*3	424	450	Fresh-water drowning (see note below).
4	440	441	Death not due to drowning.
5	547	466	Salt-water drowning.
6	612	512	Salt-water drowning.
7	540	492	Salt-water drowning.

The following is a brief description of the method of determination used.† A definite weight or volume of the blood is suitably diluted, and the protein precipitated by a solution of picric acid. The precipitate is removed by filtration, and to an aliquot portion of the filtrate is added a definite volume of silver nitrate solution of known strength. After shaking, the precipitate is allowed to settle, and the liquid filtered. The excess of silver nitrate is determined in a portion of the filtrate by means of standard potassium iodide solution.

* In the case of No. 3 carbon monoxide was also present in the blood to the extent of 50 per cent. saturation. The man, while working in a sewer, was overcome by an escape of gas, and fell unconscious into a comparatively small amount of water.

† For fuller details see "Determination of the Chloride Content of the Blood of the Heart in cases of Death by Drowning," by Gettler, *U.S.A. Naval Medical Bulletin*, May, 1922.

BENZENE POISONING.—In one case in which death was due to asphyxiation by benzene (benzol) fumes, no chemical alteration was detected in the blood, but an unusual feature was noted, namely, that the blood did not clot on keeping.

CARBON MONOXIDE POISONING.—In two cases in which death was due to gas poisoning carbon monoxide was present in the blood to the extent of 50 per cent. saturation. A case of interest to the motoring public was that in which a man was found dead sitting at the wheel of his car, which was in the garage with the engine still running. Death was found to be due to poisoning by carbon monoxide, one of the products of incomplete combustion.

Union of South Africa.

FOOD, DRUGS, AND DISINFECTANTS ACT.*

AN Act (No. 13 of 1929), which is to come into force on a date to be fixed by proclamation, is intended to "consolidate and amend the laws for regulating the labelling, and preventing the importation or sale of food and drugs which are unwholesome or adulterated, or incorrectly or falsely described, and for regulating the labelling and preventing the importation or sale of disinfectants which are incorrectly or falsely described" in the Union of South Africa.

Article 4 of the Act enumerates the conditions under which food or drugs will be regarded as adulterated or falsely described.

Articles 6 and 7 prohibit the sale of food or drugs adulterated or falsely described, or not up to the standard demanded by the purchaser, or which have been subjected to injurious abstractions, admixtures or processes.

Article 8 prohibits the importation, manufacture, or sale of any food advertised or described as specially suitable for the use of invalids or infants, which contains any preservative other than sugar or common salt.

Article 10 deals with the responsibility of the importer, manufacturer or packer of food or drugs sold in sealed original packages; and Article 11 with the inspection, sampling, analysis, and detention of imported products.

Articles 13 to 18 give special provisions relating to the sale, description, etc., of flour, meal, bread, coffee, honey, milk, and milk products.

Disinfectants imported or sold must bear a label stating (a) the name and address of the manufacturer and, when sold, of the seller; (b) full directions for use, including the proportion, strength or dilution in which it is effective; and (c) the names of its active ingredients or proportion of each, or in the case of a liquid germicide, its germicidal power or efficacy, expressed in numerical terms as compared with a standard, and as ascertained by a method prescribed by regulation (Art. 19).

The Minister is empowered to apply the provisions of the Act to any ointment, cream, powder or similar substance for use on the human skin or hair, to soap, tobacco, cigars, cigarettes, snuff, chewing gum, and any other substance.

The Minister may also make regulations prescribing the nature and composition of food and drugs, and, in general, for carrying into effect the purposes of the Act.

* From *Board of Trade J.*, 1929, p. 592. The text of the Act, which is, in the main, identical with the Bills introduced in 1927 and 1928, may be seen on application to the Department of Overseas Trade, 35, Old Queen Street, London, S.W.1.

Sulphur Dioxide in Meat.

INVESTIGATION OF THE BULLOT PROCESS FOR THE PRESERVATION OF MEAT.*

For the purpose of the investigation, the treatment of the meat intended for examination was carried out in an enclosed space having an approximate dimension of 20 ft. in length, 8 ft. in width and 7 ft. in height. Under normal working conditions, this would be sufficient for the treatment of 150 carcasses of sheep. The carcasses of one sheep, one pig, a half-side of beef, and sausages and small goods (heart, liver, kidney, etc.) were treated. The powder used in the generation of the gases was found to be of the following composition:—Saltpetre, 11; sulphur, 22; charcoal and bark, 67 per cent.; with a small quantity of essential oil.

It was particularly noticeable that where muscular tissue was exposed to the fumes, discoloration was evident to depths varying to one-half inch. Where, however, the tissue was protected with a layer of fat and skin, the penetration of the sulphur dioxide depended on the thickness of the protecting layer, as did also the discoloration (if any). The leg of pork, for instance, which was covered with a layer of fat and skin one-half inch thick, showed only very slight discoloration. It will be seen by a comparison of the results of analysis of the mutton and pork in Table I that the penetration of the sulphur dioxide is dependent on the thickness of the covering layer of skin and fat. The leg of mutton, which was covered with a thin skin only, contained 7.1 grains of sulphur dioxide per lb., while the leg of pork, protected by a half-inch layer of skin and fat, contained only 3 grains per lb. The small goods (liver, kidney, heart, etc.) which have comparatively large surfaces without a protecting skin, absorbed large quantities of sulphur dioxide (see analyses given in Table I).

Samples of treated and untreated mutton and pork were suspended under similar conditions, at room temperature, for the week 8th to 14th August inclusive). The maximum temperature during this time was 76.8° F., and the minimum temperature 47.4° F., the average mean daily temperature being 58.1° F. The treated mutton and pork appeared to be in good condition at the end of this period, but the untreated meat showed distinct signs of decomposition.

The treated beef did not keep well. As, however, it was delivered to the Laboratory in sections, the test as to its keeping qualities could not be carried out under normal conditions, since (presumably) the whole carcass is usually allowed to hang uncut until it is required for use.

Three analytical tables are appended, Table I showing the amounts of sulphur dioxide present in samples cut from different portions of the carcasses, Table II showing the loss of sulphur dioxide on keeping uncooked meat, and Table III showing the amount of sulphur dioxide lost in cooking.

* Appendix to the Annual Report of the Government Analyst for New South Wales, for the year 1928.

TABLE I.

Sulphur Dioxide Content of Meats Treated by the Bulbot Process.

Date of treatment.	Date of analysis.	Kind of meat.	Portion tested taken from	Amount taken for analysis. Grms.	Sulphur dioxide. Grains per lb.	Remarks.
7.8.28	8.8.28	Roast beef, 1st cut	*Average sample	100	10.4	Bleached where exposed to gas.
"	9.8.28	" " 2nd "	Outside meat	"	8.0	Colour normal, except where exposed to gas (small portion only).
"	"	" " " "	About 1 in. in	"	0.3	
"	"	" " " "	*Average sample	"	2.0	Sample approximately 2½ in. thick.
"	"	" " " "	Average fat	"	0.9	
"	"	Thick flank of beef	Outside meat	"	3.5	Colour normal, except small portion exposed to gas.
"	"	" " " "	About 2 in. in	"	less than	
"	"	" " " "	*Average sample	"	0.1	
"	"	Bone (beef)	*Average sample	"	1.0	
"	8.8.28	Leg of mutton	*Average sample	"	0.15	
"	9.8.28	Leg of pork	*Average sample	"	7.1	Bleached where exposed to gas.
Untreated	8.8.28	Sausages (not treated by Bulbot process)	*Average sample	"	3.0	Bleached where exposed to gas.
7.8.28	"	Sausages (similar to above and treated by Bulbot process)	*Average sample	"	2.0	Sausages as ordinarily sold, containing SO ₂ within prescribed limits, and similar to those used in experiment.
"	"	Sheep's liver, etc.	*Average sample	"	24.2	Bleached where exposed to gas.
"	"	Pig's liver, etc.	*Average sample	"	24.1	Bleached on outside.
"	"	Bullock's heart	*Average sample	"	25.2	Bleached on outside.
"	"	"	*Average sample	"	8.0	Bleached on outside.

* Average sample is a portion taken right through sample so as to represent, as nearly as possible, the whole.

TABLE II.

Loss of Sulphur Dioxide on Keeping Uncooked Meat.

Date of treatment.	Kind of meat.	Amount taken for analysis. Grms.	Date of analysis.	Sulphur dioxide. Grains per lb.	Sulphur dioxide lost in		
					2 days.	6 days.	7 days.
7.8.28	Leg of mutton	100	8.8.28	7.1	—	—	—
			10.8.28	3.6	3.5	—	—
			15.8.28	1.1	—	—	6.0
"	Leg of pork	"	9.8.28	3.0	—	—	—
			15.8.28	0.9	—	2.1	—
"	Pig's liver, etc.	"	8.8.28	25.2	—	—	—
			10.8.28	14.2	11.0	—	—
"	Sausages (treated)	"	8.8.28	24.2	—	—	—
			10.8.28	23.4	0.8	—	—

The mutton and pork were exposed to the air; the pig's liver and sausages were kept loosely wrapped in paper.

TABLE III.
Sulphur Dioxide in Meat Lost in Cooking.

Date of treatment.	Date of analysis.	Kind of meat.	Amount taken for analysis. Grms.	Weight.		Sulphur dioxide. Grains per lb.		Remarks.
				Before cooking. Grms.	After cooking. Grms.	Uncooked meat.	Cooked meat.	
7.8.28	10.8.28	Leg of mutton	100 uncooked 76 cooked	140	76	3.6	2.5	Cooked by gentle boiling for 1 hour with approx. 4 parts of water.
„	15.8.28	„	100 uncooked 100 cooked	—	—	1.1	0.6	Baked. Weight 2-3 lb.
„	10.8.28	Sausages (treated)	100 uncooked 90 cooked	141	95	23.4	20.2	Cooked by frying for 20 minutes; when cooked had acid taste and odour of SO ₂ .
„	10.8.28	Pig's liver, etc.	100 uncooked 94 cooked	138	94	14.2	6.5	Cooked by gentle boiling 1 hour with approx. 4 parts of water.

Taking into consideration the loss in weight in cooking, the actual amount of sulphur dioxide lost represents two-thirds of the total in boiling and one-third in frying.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Modification of the Fiehe Test for the Detection of Artificial Invert Sugar in Honey. E. K. Nelson. (*J. Assoc. Off. Agric. Chem.*, 1929, 12, 323-324.)—A solution of 2 grms. of sample in 10 c.c. of water is extracted rapidly with ether in a Palkin and Watkin's apparatus for 30 minutes, the extract concentrated to 5 c.c., 2 c.c. of a fresh 1 per cent. solution of resorcinol in concentrated hydrochloric acid added, and the mixture immediately shaken. After 5 minutes pure honey gave a very faint pink, whilst in the presence of 10 to 20 per cent. of invert sugar a deep pink to dark red colour was obtained. Re-extraction of the residues showed that all the oxymethyl furfural had been removed. J. G.

Detection of Fruit Wine in Grape Wine. B. Bleyer and W. Diemair. (*Chem. Ztg.*, 1929, 53, 621, 641-642.)—The following modification of Werder's method (*ANALYST*, 1929, 422, 476) is reliable for the detection of 10 per cent. of fruit wine in grape wine:—The wine (100 c.c.) is shaken with 7 grms. of pure animal charcoal for 20 minutes, heated, filtered hot and evaporated under reduced pressure

in Werder's apparatus (*loc. cit.*). When 5 c.c. remain, the hot liquid is centrifuged to remove any deposit of tartar, and evaporated further to a syrup (1.2 to 1.5 grms.). This is shaken for 1 hour with 0.2 c.c. of benzaldehyde and 1 c.c. of sulphuric acid (1:1), and the crystals allowed to separate over-night. Dibenzal mannitol forms fine needles, whereas dibenzal sorbitol is an amorphous gelatinous mass. The corresponding triform acetals are needle-shaped crystals, m.pt. 227° and 206° C., respectively; they are prepared from a solution of the precipitate by the action of equal weights of formalin and concentrated hydrochloric acid heated under a reflux condenser for 1½ hours. J. G.

Determination of Carotin in Flour. C. G. Ferrari and C. H. Bailey. (*Cereal Chem.*, 1929, 6, 347-371.)—The authors criticise the tentative method of the A.O.A.C. on the grounds of its inability to yield consistent results, owing to the presence of invisible suspended matter in the filtered petroleum spirit solution of carotin. By increasing the efficiency of filtration with paper pulp or unglazed porcelain low results are obtained, since a portion of the carotin is adsorbed by the filtering media. The following modification is claimed to yield reliable results, although approximately 20 per cent. of the carotin is retained by the flour, the remainder only being actually determined:—Twenty grms. of the sample are weighed into a glass-stoppered bottle, and 100 c.c. of petroleum spirit are added from a pipette. After agitation at frequent intervals the mixture is allowed to stand in a dark place over-night, and the supernatant liquid is siphoned off and filtered in the following manner. An alundum thimble is fitted by means of a rubber ring into a glass adapter, the stem of which is passed through a rubber stopper in the lid of a vacuum desiccator containing a little petroleum spirit to saturate the atmosphere. The thimble is rinsed several times with small portions of the carotin solution, each portion being drawn through under a slight vacuum. A graduated cylinder is then placed under the adapter, and 50 c.c. of the carotin solution are filtered slowly, the thimble being filled to a depth not exceeding 5-6 mm. The transmittancy of a 10 cm. depth of the solution is then determined in a spectrophotometer using a wave-length of 4358 Å. derived from a mercury vapour lamp, and is compared with that of a petroleum spirit solution of pure carotin. Experiments have shown that corresponding results are obtained if the petroleum spirit is replaced by "gasolene," the latter having the advantages of lower volatility and lower price. The use of filtering media may be avoided in the determination by the following method, which, however, occupies a longer time. After agitation as described in the previous method the mixture is allowed to stand in darkness for 48 hours, and the supernatant liquid is slowly separated by means of a capillary syphon. Details are given of the precautions necessary in transmittancy measurements, the effect of altering the ratio of weight of sample and the volume of solvent, and the influence of various milling products, such as bran and shorts, upon the results. Tables showing the results obtained with different varieties of Canadian wheat and various products obtained in milling are given. (Cf. ANALYST, 1927, 52, 446.) T. J. W.

Separation of Solid Fats into their Constituents. **A. Van Raalte.** (*Rec. Trav. Chim. Pays Bas*, 1929, **48**, 1058–1060.)—Lund's work (*Z. Unters. Nahr. Genussm.*, 1922, **44**, 113) on the relation of the proportions of fatty acids in a fat to the sp. gr., refractive index, iodine, saponification and acetyl values is criticised in that it provides no means of distinguishing between fats containing the same fatty acids attached to different hydroxyl groups of the glycerol molecule. A method is proposed for solid fats in which the crystalline portion of the fat is removed from the amorphous portion by shaking 10 grms. of the solid fat with 10 c.c. of 96 per cent. alcohol and sufficient acetone (20 to 30 c.c.) to coagulate the crystals. The amorphous fat dissolves at ordinary temperatures, and may be removed by filtration, the crystals being washed twice with 20 c.c. of a mixture of equal volumes of alcohol and acetone, the filtrate evaporated, and the residue dried and weighed. Mutton tallow, beef fat, horse fat, and lard, yielded 4.8, 3.6, 5.4, and 6.6 grms. of liquid phase, respectively, the refractive indices (40° C.), aniline points (temperature of separation of a mixture with aniline), and iodine values of which were shown to be considerably higher, lower and higher, respectively, than those of the corresponding solid phases. J. G.

American Reindeer Fat. **W. F. Baughman, G. S. Jamieson and R. S. McKinney.** (*Oil and Fat Ind.*, 1929, **6**, 11–12.)—The analysis of five samples of reindeer fat taken from different parts of two carcasses gave the following figures:—M. pt., 45.8–48.6° C.; sp. gr. at 40°/25° C., 0.8981–0.8993; n_D^{20} , 1.4510; saponification value, 194.3–199.2; iodine value (Hanus), 33.7–39.4; acetyl value, 5.0–8.0; Reichert–Meissl value, 0.0–0.3; Polenske value, 0.3–0.5; unsaponifiable matter, 0.4 per cent.; acid value, 2.0–8.6; saturated acids, 53.6–59.9 per cent.; unsaturated acids, 41.4 per cent. (of iodine value, 90.0). The composition of the fat was: Oleic acid, 36.8; myristic, 6.7; palmitic, 35.0; stearic, 20.5; and arachidic acid, 0.7 per cent. D. G. H.

Fatty Oil of the "Pilgrim" Whale (*Cetorhinus Maximus*, Günner).
Biological Relations between the Cholesterols and Squalene. **E. André and H. Canal.** (*Bull. Soc. Chim.*, 1929, **45–46**, 498–511.)—The oil of a young male specimen of this whale (sp. gr. 15/0° C. 0.9105, n_D^{20} 1.4865, $[\alpha]_D^{20}$ – 6° 54', saponification value 98.7, Hanus iodine value 155.2, acidity 0, acetyl value 0) represents only 6 per cent. of its weight, whereas the yield from an adult is 12.5 per cent. (*id.*, 1927, **41**, 921). After saponification it yielded 40.5, 58.5 and 3.21 per cent. of unsaponifiable matter, fatty acids and glycerol, respectively. The first was divided into two portions by alternate treatment with acetone and petroleum spirit. One was crystalline and was shown, by m.pt. and iodine value determinations of the products obtained by fractional crystallisation from petroleum spirit, to contain 3 parts of ordinary cholesterol, $C_{27}H_{46}O$, and one of a cholesterol having two ethylenic linkages (iodine value 133.0). It represented 22.5 per cent. of the weight of the oil, and is the largest quantity of cholesterol obtained from any animal oil or fat. The other (liquid) portion was fractionally distilled and found

to consist of 1 part of pristane, $C_{18}H_{38}$ (Tsujiimoto, *Ann. de Chim.*, 1927, 7, 69) and 4 parts of squalene. Bromination experiments with the latter confirmed the authors' opinion (*loc. cit.*) that the addition of hydrogen bromide gas does not proceed to completion, and experiments with iodine bromide indicate the formula $C_{27}H_{44}$ for squalene. Separation of the fatty acids by Tsujiimoto's method (*loc. cit.*), and by fractional crystallisation of the lead and lithium salts, led to the identification of 15 per cent. of arachidonic acid, myristic acid (20 per cent.), cetoleic acid (55 per cent.), and therapeutic acid, $C_{18}H_{36}O_2$ (10 per cent.), of which 32 per cent. was in the form of glycerides, while the remainder was combined as esters and cholesterol. The transformation—fatty acids— \rightarrow cholesterols— \rightarrow squalene—indicated by these figures corresponds with the increase in maturity of the animal and suggests a close chemical and physiological relationship between squalene and cholesterol (*cf.* following abstract). Further, the presence of a high proportion of hydrocarbon mixed with alcohols having a high optical rotation supports the theory of the marine origin of petroleum.

J. G.

Marine Animal Oils. Oil of *Centrophorus Granulosus*. E. André and H. Canal. (*Bull. Soc. Chim.*, 1929, 45–46, 511–524.)—The methods outlined in the preceding abstract were applied to the unsaponifiable matter of the oils extracted from the eggs, of foetus oil, and of the fat of adult animals. The eggs yielded 29.6 per cent. of a brown oil containing 43.5 per cent. of fatty acids with high molecular weight and iodine value, 4.7 per cent. of a mixture of at least two cholesterol alcohols of which one had two ethylenic linkages (*cf. loc. cit.*), 50.4 per cent. of a mixture of highly unsaturated hydrocarbons (squalene), and 3.9 per cent. of glycerol. A similar oil appeared in the foetus fat, except that the fatty acids and cholesterol alcohols were less, and the hydrocarbons greater in quantity. The fats of growing and adult animals yielded unsaponifiable matters rising progressively to 91 per cent. in the latter case, and were composed principally of highly unsaturated hydrocarbons derived from the glycerides of the fatty acids of the clupanodonic series, the cholesterol alcohols being intermediate products (*cf. loc. cit.*). This transformation of clupanodonic glycerides into cholesterol and then into hydrocarbons may be followed progressively from the composition of the oils from the egg and foetus and of the fats of the young and adult animals.

J. G.

Thiocyanogen Value of Strophanthus Oil and of Oils of the Chaulmoogra Group. E. I. Van Itallie. (*Pharm. Weekblad*, 1929, 66, 677–683.)—Kaufmann's determination of the thiocyanogen value (T) (*ANALYST*, 1928, 53, 613) has been applied to the oil extracted by petroleum spirit from *Kombé strophanthus* (sp. gr. 0.9270; n_D^{20} , 1.4701; acid value, 19.0; saponification value, 193.5, Wijs iodine value I , 95.1, T 67.4). The percentages of linolic, oleic and saturated acids were then calculated from the accepted values of R and T for linolic and oleic acids by means of the expressions $1.104(I-T)$, $1.112(2T-I)$ and by difference, respectively (*cf.* Matthes and Rath, *Arch. Pharm.*, 1914, 683), and found to be 30.5, 44.3 and 25.2 per cent., respectively.

For samples of chaulmoogra and hydnocarpus oils the values I 100.6 and 95.7 and R 99.1 and 94.8 were found, respectively (*cf.* Hashimoto, *ANALYST*, 1925, 50, 566; Bömer and Engel, *id.*, 1929, 423). The presence in chaulmoogric acid, $C_{18}H_{32}O_2$, of an asymmetric carbon atom attached to an unsaturated cyclic residue was also confirmed.

Gorli-oil, obtained from the African tree *Oncoba echinata* (André and Jouatte, *ANALYST*, 1928, 53, 604) contained 10 to 12 per cent. of the highly unsaturated acid $C_{18}H_{30}O_2$, and had m.pt. $40^\circ C.$, n_D^{40} 1.4722, $[\alpha]$ 49.02, I 93.4, acid value 5.6, saponification value 200.4, T 93.2.
J. G.

Composition of Wool Fat. J. C. Drummond and L. C. Baker. (*J. Soc. Chem. Ind.*, 1929, 48, 232–238T.)—Crude merino wool was extracted with light petroleum, yielding crude fat which contained only small quantities of free fatty acids or alcohols and consisted largely of the fatty acid esters of the higher aliphatic alcohols, and of cholesterol and ischolesterol. No glycerol was present and only negligible traces of nitrogen or phosphorus-containing fatty substances. The fatty acids consisted almost entirely of the saturated acids, cerotic, palmitic and stearic, and no evidence of high oxygen acids was obtained. The unsaponifiable matter consisted of cholesterol, ischolesterol and higher aliphatic alcohols. Isocholesterol was separated from cholesterol by removing the latter with digitonin, and no other method was found satisfactory. It had a m.pt. of 139 – $140^\circ C.$ and $[\alpha]_D +84^\circ$. The colour reactions resemble those of certain sterols. The compound is unsaturated, but the degree of unsaturation is not yet established. It is not readily reduced by hydrogen in presence of palladium, and more work is required to establish the formula. The name ischolesterol is misleading, and lanosterol is suggested. Ergosterol was not found in the unsaponifiable matter.
D. G. H.

Rapid Method for Quinine Determination. G. A. Sticht. (*Chemist Analyst*, 1929, 18, [iii], 6–7.)—In the case of cinchona bark 66.667 grms. of 40-mesh powder are shaken continuously for 2 hours, or intermittently for 6 hours, with 50 c.c. of 20 per cent. ammonia and 501 c.c. of a mixture of 105 c.c. of chloroform and 420 c.c. of toluene at $20^\circ C.$, and 250 c.c. filtered through cotton wool. The filtrate is then shaken thoroughly, but not violently, with 25, 20 and 20 c.c. successive portions of 15 per cent. sulphuric acid, the combined extracts evaporated at a low temperature to 50 c.c., gently boiled, and ammonia added until the solution is slightly alkaline to methyl orange. A solution of 6 grms. of citric acid in 10 c.c. of water is made slightly alkaline to phenolphthalein with sodium hydroxide solution, boiled and added to the hot extract, and the acid quinine citrate, which separates on cooling, is filtered off in a Gooch crucible, washed with 70 c.c. of water, dried at $100^\circ C.$, and weighed. The factor 3×0.6279 gives the percentage of anhydrous quinine, and the herepathite test may be used to confirm the purity of the precipitate. Other alkaloids may be determined in the wash-liquors.
J. G.

Identification of Atropine by means of Wagner's Reagent. C. C. Fulton. (*J. Assoc. Off. Agric. Chem.*, 1929, 12, 312-317.)—Wagner's test gives the following types of atropine crystals increasing in size in the order given according as 2.75, 8, 35 and 50 grms. of potassium iodide, respectively, are used in the presence of 1 gm. of iodine and 100 c.c. of water:—(1) Small red-brown rods, (2) small yellow plates, (3) a mixture of yellow and dark red crystals, (4) orange-red, hexagonal, elongated plates with dark-red diamond-shaped or triangular grains and a few yellow cubes. The corresponding optimum ranges of concentration of the test solution are 1:5,000 to 1:50,000, 1:800 to 1:5,000, 1:650 to 1:2,000, and 1:200-1:800, respectively, but the first reagent has been found to give a positive reaction with a 1:200,000 solution of atropine. Hyoscyamine was found to give similar crystals, and one sample of atropine gave crystals of abnormal shape. J. G.

Assay of Jalap. L. E. Warren. (*J. Assoc. Off. Agric. Chem.*, 1929, 12, 324-332.)—Comparative trials of six methods led to the rejection of the U.S. Pharmacopoeia X and Jenkins' methods on account of the high results obtained, and of other methods involving the use of aliquot portions. Dale's method was found accurate but tedious, and the following is recommended:—The drug is ground to a No. 60 powder, and 10 grms. extracted with 50 c.c. of alcohol for 30 minutes under a reflux condenser, and then percolated with warm alcohol till 100 c.c. of tincture are obtained. Of this, 25 c.c. are evaporated and extracted for 2 minutes with 15 c.c. portions of boiling water until no more colour is removed. The residue, after filtration, is extracted thoroughly with warm alcohol, the extract evaporated, and the resin dried to constant weight at 100° C. J. G.

Keeping Properties of Digitalis and some of its Preparations. H. B. Haag and R. A. Hatcher. (*Amer. J. Pharm.*, 1929, 10-11, 474-480.)—There is no evidence that ground digitalis leaf deteriorates during a period of many years if kept with reasonable care. Fluid extracts and tinctures of digitalis decompose but slowly, and at somewhat variable rates, and infusions at a slightly more rapid rate, but the latter may be used with confidence for several weeks. No toxic substances develop during deterioration, and dosage may be increased to correspond with the degree of deterioration. Probably a substance causing decomposition of some active principles is present in digitalis, itself being decomposed in the process, and there is also a substance resisting deterioration. Very old tinctures have nearly 70 per cent. of the activity of average fresh tincture of good quality. Acidity is not the chief factor in decomposition, nor is a low alcohol percentage the sole cause. Ampoules should be made of a glass containing a minimum amount of soluble alkali. D. G. H.

Determination of Nitrate Nitrogen in Tobacco. H. B. Vickery and G. W. Pucher. (*Ind. Eng. Chem. Anal. Edit.*, 1929, 1, 121-123.)—Two portions of 5 grms. of the powdered tobacco are placed in separate flasks, 30 c.c. of water and 5 c.c. of 50 per cent. sodium hydroxide solution are added to each, and the mixtures are submitted to steam distillation, 800 c.c. of distillate being collected

in receivers containing hydrochloric acid. These distillates may be used for the determination of the nicotine by the silicotungstic acid method. The contents of the flasks are then diluted to 25 c.c., 15 c.c. of sulphuric acid (1:1) are added to each, and to one flask 3 grms. of reduced iron are added. The mixtures are boiled for five minutes, diluted to 200 c.c., treated with 35 c.c. of 50 per cent. sodium hydroxide solution, and distilled. The difference between the amounts of ammonia found in these distillates is a measure of the nitrate nitrogen in the tobacco. The control determination described above cannot be avoided, since a small quantity of ammonia is always formed when the sample is heated with sulphuric acid.

W. P. S.

Quantitative Analysis of Certain Medicinal Preparations containing Mercury. A. Jonesco-Matiu and A. Popesco. (*Ann. Chim. analyt.*, 1929, 11, 225-231.)—The method depends upon the titration of the mercury ion by the chlorine ion after transformation into mercuric sulphate and precipitation by sodium nitroprusside, and is now extended to the determination of calomel, corrosive sublimate, mercuric ammonium chloride, mercury ointments, mercuric iodide, grey ointment, and iodide ointments. For example, 1 grm. of corrosive sublimate is dissolved in 80 c.c. of water, made up to 100 c.c., and the mercuric oxide precipitated from a known volume with 40 per cent. sodium hydroxide, the solution centrifuged, and the precipitate washed, dissolved in concentrated sulphuric acid, transferred to 80 c.c. of water, 12 drops of sodium nitroprusside solution added, and then 0.1 N sodium chloride solution, until the cloudiness disappears. In the case of ointments 10 c.c. of sulphonitric oxidising mixture are added, and the organic matter destroyed, after which crystals of mercuric sulphate are deposited; or the fat may be dissolved in ether and the mercury collected by centrifuging.

D. G. H.

Biochemical.

Storage of Manganese and Copper in the Animal Body and its Influence on Haemoglobin Building. R. W. Titus and J. S. Hughes. (*J. Biol. Chem.*, 1929, 83, 463-467.)—The fact that young rats from mothers fed on a whole wheat-milk powder diet became anaemic much more rapidly than young rats from mothers on a more complex ration suggested to the authors the probability of a prenatal supply or storage of the haemoglobin-building elements. Titus, Cave and Hughes (*J. Biol. Chem.*, 1928, 80, 565) showed that manganese, as well as copper, is effective in the utilisation of iron in haemoglobin building. Data presented now show that both manganese and copper are apparently stored in the animal body when these mineral supplements are added to the ration, and that manganese, as well as copper, when given as food or stored in the animal body, is effective in the utilisation of iron in haemoglobin building. Young rats fed on milk supplemented with manganese chloride, and others fed on milk supplemented with copper sulphate, showed a gradual decrease in the haemoglobin content of their blood until the time the manganese or copper supplement was discontinued. On the addition then of an

iron supplement the haemoglobin content of the blood began to increase until it became almost normal. A third lot of rats on milk supplemented with iron for the entire experimental period gradually became anaemic, but not so quickly as when no iron was added as a supplement. It is possible, therefore, that the animal is able to utilise a small amount of iron, owing, not to copper or manganese as an impurity in the food, but rather to a prenatal storage of these elements in the body. The experimental data are shown in graphic form. P. H. P.

Excretion of Lead in Urine. H. Millet. (*J. Biol. Chem.*, 1929, **83**, 265–268.)—Recent work by various workers on the excretion of lead has shown that the major part of the excretion is found in the faeces, and that healthy men, many of whom have had no definite exposure to lead, excrete lead normally in urine and faeces. An investigation has now been carried out which deals with the determination of the total lead excreted in the urine of (a) a few healthy persons, (b) a number of cancer patients who had received intravenous injections of colloidal lead phosphate, and (c) cancer patients resident in the same nursing home, who had not been treated with lead. Lead was determined electrometrically as lead ion by the use of a fluid lead amalgam electrode, operated in the absence of oxygen, as recently described by Millet (*Tr. Faraday Soc.*, 1929, **25**, 147). The electrometric method is accurate to about 2 per cent., but, owing to the risk of contamination with lead in the treatment of the urine, the accuracy of the determinations may be lessened. The treatment of the urine was based on the work of Fairhall (*J. Biol. Chem.*, 1924, **60**, 485; *ANALYST*, 1924, **49**, 490), who found that ammonia precipitates practically all the lead from urine. The tabulated results show that there is a definite normal excretion of lead in urine. In cancer patients who had received the injections of a lead phosphate colloid, and in cancer patients not treated with lead, the excretion was about the same, and averaged about 0.085 mgrm. of lead per litre. The average figure found is the same as that recorded for healthy persons by Kehoe, Edgar, Thamann and Sanders (*J. Amer. Med. Assoc.*, 1926, **87**, 2081), whose method was less accurate. There is no evidence that the lead injected was at any time being excreted in the urine. Single doses of the lead phosphate colloid contained usually 50 mgrms. of lead, and thus an increase above the normal level of excretion would be expected to appear if the lead injected was being excreted through the kidney. It may be mentioned that lead phosphate, which is very insoluble, produces practically no toxic symptoms, and damages the kidney very little. P. H. P.

A Previously Undetected Constituent of Blood. E. W. Rockwood, R. G. Turner and J. J. Pfiffner. (*J. Biol. Chem.*, 1929, **83**, 289–297.)—A previously undetected substance, which reduces arsenophosphotungstic acid, is shown to be present after acid hydrolysis of the blood of man, dog and rabbit. It is also found in the muscle, kidney and liver of dog and rabbit. In the few ox and pig bloods examined it was detected only in traces. This substance has provisionally been named substance Z. A method is described for its determination in tungstic acid blood and tissue filtrates, and its amounts have been determined in

normal and various pathological bloods. In protein-free tungstic acid blood filtrates, uric acid, thioneine and substance Z are present, and all give the same blue colour with alkaline arsenophosphotungstate. Acid hydrolysis of the protein-free filtrate liberates uric acid, and it is now shown by the authors that acid treatment of the thioneine fraction increases the material measured by the arsenophosphotungstate reaction, and thus produces substance Z. Therefore to determine the quantities of uric acid, thioneine and substance Z in blood, oxalated blood was used, and four colorimetric determinations were made on each sample: (1) uric acid direct, (2) uric acid indirect, (3) thioneine plus substance Z, and (4) thioneine. A part of the blood filtrate was hydrolysed with sulphuric acid, a part was not so treated; uric acid, both direct and indirect, was determined in the unhydrolysed portion. Substance Z is freed by acid hydrolysis and is then precipitated by silver lactate, but is not afterwards liberated by acid sodium chloride solution. Therefore it was determined with thioneine in the silver residue from the hydrolysed portion. Thioneine was similarly determined in the unhydrolysed portion, and the amount of substance Z was found by subtraction. All tissue filtrates were prepared from the warm organs according to the method of Folin, Berglund and Derick (*J. Biol. Chem.*, 1924, **60**, 361). In a discussion it is shown that substance Z is not the same as any of the known constituents of tungstic acid blood and tissue filtrates.

P. H. P.

Quantitative Changes in the Chloroplast Pigments in the Peel of Bananas during Ripening. H. von Loesecke. (*J. Amer. Chem. Soc.*, 1929, **51**, 2439-2443.)—An investigation was undertaken to gain some knowledge of the changes which the pigments in banana peel undergo when the fruit is ripening (changing from green to yellow), and of the cause of the yellow colour. The three pigments, chlorophyll ($a+b$), xanthophylls and carotin were determined. Other pigments are present, as during the separation process there were indications of flavones and anthocyanins, but these latter are present in the cell sap, whilst chlorophyll, xanthophylls and carotin are present only in the specialised portions of the protoplasm known as plastids. The fruit was peeled, the pulp side of the peel scraped free from pulp, and the peel then cut into small pieces and ground in a mortar with sand. It was extracted in the cold with 30 per cent. aqueous acetone to remove gums and flavones. The chloroplast pigments were then extracted with pure acetone after the method of Schertz (*Plant Physiology*, 1928, **3**, 211). The extracted chlorophylls were saponified to chlorophyllins, and determined colorimetrically with a solution of chlorophyllins prepared from pure chlorophylls as a standard. Xanthophylls and carotin, after extraction and separation from the chlorophylls, were determined colorimetrically with the use of a solution of naphthol yellow as a standard for the former, and naphthol yellow and orange G as a standard for the latter, after the method of Sprague (*Science*, 1928, **67**, 167). The comparisons with these dyes could not be made by artificial light. The percentages of total sugar (as invert) were determined on the pulp of the fruit from which the peel was taken. This is the best criterion of the ripeness of the fruit. From the data obtained the following conclusions have been reached:—The

chlorophyll content of the peel ranges from 102.9 to 51.7 mgrms. per kilo. of fresh peel in the unripe fruit at discharge from the boat, and decreases as the fruit ripens. Chlorophylls decrease as a straight line function of time. The total yellow pigments (xanthophyll plus carotin) remain approximately constant throughout the maturation of the fruit; therefore the yellow colour of an unripe banana is masked by chlorophyll. The amount of xanthophylls is always greater than the amount of carotin, the range of the former being from about 5 to 7 mgrms. per kilo. of fresh peel, whilst the range of the latter is from 1.5 to 3.5 mgrms. per kilo. of fresh peel.

P. H. P.

Antimony Trichloride Colour Test for Vitamin A. N. Evers. (*Quarterly J. Pharm.*, 1929, 2, 227-237.)—In normal cases the author recommends the addition of 2 c.c. of reagent, made from recrystallised antimony trichloride and less than a month old, to 0.2 c.c. of a mixture of 2 c.c. of oil and 8 c.c. of dry chloroform. The colour is read in the tintometer in a 1 cm. cell exactly 30 seconds after the addition of the last drop of reagent, and 85 times the number of blue units gives the units of vitamin A per grm., corresponding approximately with the U.S.P. biological unit. If necessary, the quantity of oil used should be altered so as to obtain a colour of between 4 and 6 blue units, and the factor adjusted accordingly. The quantity of sample taken is of particular importance with highly active fats such as ox liver fat, 0.0005 mgrm. of which gave a distinct colour, but any error involved when small quantities of sample are used may be minimised by the addition of sufficient inactive oil (e.g. arachis oil or ox liver fat irradiated so as to destroy the vitamin) to bring the total oil concentration to 2 per cent. The natural colour of ox liver fat appears to modify the relation of the colours obtained from two different quantities of the fat.

J. G.

Comparison of Biological and Colorimetric Assays for Vitamin A as Applied to Fish Oils. E. R. Norris and I. S. Danielson. (*J. Biol. Chem.*, 1929, 83, 469-475.)—All evidence so far published seems to indicate that the colour produced with arsenic trichloride, or with the chloroform solution of antimony trichloride, with oils, is associated with the vitamin A content of the oil tested, but no exact data are available to show a quantitative relationship between the colour produced by either of the above reagents and feeding experiments on the oils. The colour reaction of a series of six fish body and fish liver oils with antimony trichloride has now been studied, and an attempt made to correlate the colour with careful feeding experiments which had been made on each oil. The solution of antimony trichloride in chloroform was cooled to the temperature of ice-water (2 to 4° C.), and allowed to remain until equilibrium was reached, when a clear solution was obtained which contained about 18 per cent. (weight/volume per cent.) of antimony trichloride; this permitted the use of lower temperatures than room temperature under ordinary laboratory conditions, for a long enough period to obtain an accurate reading. A series of dilutions of cod-liver oils, ratfish liver oil, chinook, sockeye, silver, and humpback salmon body oils, was prepared in chloroform. To measure each dilution 0.3 c.c. of it was placed in

a cell in a Lovibond tintometer, 3 c.c. of the cooled reagent added (mixing being accomplished by delivering the reagent in a strong stream into the cell), and the colour produced after 10 to 15 seconds matched with standard Lovibond units; a reading was taken at the end of 30 seconds. Figures show the results obtained when the intensity of the colour produced is plotted against the mgrms. of oil used in the reaction. It is definitely concluded that the blue colour produced by a fish oil and antimony trichloride reagent is not proportional to the amount of oil used; therefore it is not directly proportional to the vitamin A content, if the colour reaction is produced by this factor. At no concentration is the curve obtained with varying amounts of cod-liver oil in antimony trichloride reagent linear. However, the curves approach a straight line at very low colour values, so that, by plotting the lower values on a larger scale, the amount of each oil required to give the same colour as that obtained with 0.00099 grm. of cod-liver oil (1 animal unit which = 2.18 Lovibond blue units) may be read on the abscissa. These values, given to the nearest 10 mgrms., are shown to agree fairly well with those obtained biologically. Therefore the colorimetric assay upon the fish oils tested agrees within reasonable limits with the biological assay when the technique described is used.

P. H. P.

Improvements in the Method of Isolating the Anti-Beri-Beri Vitamin.

B. C. P. Jansen. (*Rec. Trav. Chim. Pays Bas*, 1929, **48**, 984-985.)—By replacing the phosphotungstic acid by silicotungstic acid and the alcoholic solution of platinum chloride by a solution of cadmium chloride in the original method (Jansen and Donath, *Mededeel. Dienst Volksgezondheid Nederlandsch-Indië*, 1927) the yield of anti-beri-beri vitamin from rice bran may be doubled.

D. G. H.

Bacteriological.

Rapid and Accurate Method for Determination of the Quantity of Yeast or other Micro-Organisms in a Suspension. **R. J. Williams, E. D. McAlister and R. R. Roehm.** (*J. Biol. Chem.*, 1929, **83**, 315-320.)—Recent methods described for the determination of yeast crops have all been tried, but none has been found highly satisfactory; their disadvantages are outlined. The authors have devised a new method which can be used not only to determine yeast crops, but also to standardise very dilute suspensions for seeding. This method involves the interposing of the yeast suspension in a suitable cell between a 6 to 8 voltage light and a specially prepared thermo-couple, and determination of the E.M.F. set up by the thermo-couple. An inexpensive galvanometer is sufficiently sensitive to allow an accurate determination of the amount of yeast in suspension. A weighed quantity of starch-free baker's yeast (69.5 per cent. moisture) was suspended in 0.08 M sugar solution, and 14 different dilutions were prepared from the original. Each of the suspensions was interposed (with the same cell) and the galvanometer deflections recorded. By changing slightly the resistance in series with the lamp to compensate for the slow drop in the battery voltage, a constant deflection was maintained when a cell of distilled water was interposed. The

galvanometer showed very little "zero creep" after the thermo-couple had been illuminated for a short time. The curve obtained (yeast in suspension: galvanometer deflections in cm.) is shown. Unknown samples, prepared by one author and tested by another, gave very good results. Details are given of the apparatus required, its arrangement, and the preparation of the thermo-couple. That used in this work consists of a receiver of foil (tin or platinum, blackened on the side exposed to the radiation), and two small wires, one of bismuth and the other an alloy of bismuth and tin (95.5 per cent. Bi, 4.5 per cent. Sn by weight). These are "spot welded" together, and to the centre of the receiver in one operation, and their other ends are welded (or soldered) to two relatively heavy copper leads. The junctions of the two wires with the receiver is the hot-junction of the thermo-couple, and their junctions with the copper leads constitute the cold junction. The couple should be inclosed in an air-tight container of glass. This new method is rapid, accurate, and can be used over a very wide range of concentrations. Apart from its use with yeast, the apparatus can be used to determine the quantities of bacteria or other organisms in suspension (possibly quantitatively suspended matter of various kinds), and hence should be a very useful tool in the field of biochemistry.

P. H. P.

Organic Analysis.

Use of Aldehydes and Di-hydroxy Acetone in the Detection and Differentiation of Phenols. A. H. Ware. (*Quarterly J. Pharm.*, 1929, 2, 249-253, 254-264, 265-266.)—(1) The phenol (0.05 gm.) is dissolved in 3 c.c. of concentrated sulphuric acid, 1 drop of 10 per cent. oxantin (di-hydroxy acetone) solution added, and any colour-change noted. Five per cent. hydrobromic acid is then added, a drop at a time, until the maximum colour change is reached, and finally water is added in the same way and any further change noted. (2) A crystal of tartaric acid, smaller than a pinhead, is gently warmed with a solution of 0.05 gm. of the phenol in the concentrated acid until fumes appear, and the colour noted. (3) To obtain the greatest amount of differentiation, 2.5 c.c. of a mixture of 1 c.c. of formalin and 99 c.c. of concentrated sulphuric acid are mixed with 2.5 c.c. of a sulphuric acid solution of the phenol (0.01 to 0.05 gm.). Water is added, drop by drop, the mixture shaken, and the colour-change noted. If a dark precipitate is obtained, it is best to add the mixture slowly to 6 c.c. of alcohol. The three following tests are more suited to mixtures of phenols with other substances. (4) An extract of the sample (free from alcohol and resin) in 10 c.c. of 0.5 to 7.5 *N* hydrochloric acid, diluted if possible till almost colourless, is precipitated with 5 drops of formalin at the boiling-point, cooled, re-heated and cooled, and the precipitate filtered off from the hot solution. The precipitation or otherwise of a particular phenol, the rate of reaction, the colour of the precipitate, and its solubility in alcohol or 5 per cent. aqueous alkali depend on the nature of the phenol, the strength of acid, the time and the temperature, and qualitative separations and differentiation tests for phenols based on these lines are tabulated. (5) Di-hydroxy acetone may replace formalin in acid solutions not weaker than 7.5 *N*,

but this reagent is less suitable for separation purposes. A better colour is often obtained by the addition of a few drops of hydrogen peroxide at the moment the colour change appears. (6) Stain tests may be carried out with a deal shaving dipped in the solution, dried, dipped in hydrochloric acid and gently warmed. Or a solution of 0.01 grm. of phenol in 1 c.c. of alcohol, with 1 drop of formalin or dihydroxy-acetone solution is allowed to fall on 2 filter papers, one above the other, on a warm tile, and 5 drops of strong hydrochloric acid added while the papers are still slightly moist. The colour changes are noted when the papers are almost dry, again after addition of 1 drop of hydrogen peroxide and 2 more drops of acid, and finally after addition of ammonia. The results of each test are summarised for a number of phenols. Cresol in carbolic acid is detected by the gradual admixture in the cold of 5 drops of phenol solution with a mixture of 2 drops of a 2 per cent. alcoholic solution of vanillin and 5 c.c. of hydrochloric acid. A rose-pink colour is given by 1.5 per cent. or more of ortho- or meta-cresol, or both, within 3 minutes. If the mixture is then poured into potassium hydroxide solution, the colour will be intensified if ortho-cresol is present (*cf.* ANALYST, 1927, 52, 335). J. G.

Determination of Phenols. J. A. Shaw. (*Ind. Eng. Chem., Anal. Edit.*, 1929, 1, 118–121.)—A special method of steam-distillation is described, the phenols being determined subsequently by means of the turbidity produced by the addition of bromine. Ten c.c. of the sample, which may contain up to 0.1 per cent. of phenols, are placed in a test-tube and acidified with a few drops of dilute sulphuric acid. The test tube is closed with a cork and connected by suitable tubes with a condenser and a second test-tube containing water. Both test-tubes are placed in a steam chamber and heated at 100° C. A current of air is then blown through the tubes, passing first through the test-tube containing water, then through the test tube containing the sample, and thence to the condenser. When 25 c.c. of distillate have been collected, small portions of it are diluted successively until the concentration of the phenol is reduced to about 35 parts per million. A portion of the diluted distillate is then treated with bromine water, and the turbidity produced compared with those obtained by treating known amounts of phenol with bromine. These standards may conveniently contain from 30 to 35 parts of phenol per million, and the comparisons should be made at 20° C. Alcohols, amines, aldehydes, organic bases, oils and inorganic salts interfere and must be removed before the phenol is determined. W. P. S.

Identification of Primary Phenylethyl Alcohol in Essential Oils and Mixtures of Perfumes. S. Sabetay. (*Ann. Chim. Analyt.*, 1929, 11, 193–195.)—The fraction corresponding to phenylethyl alcohol is slowly distilled with coarsely powdered potassium hydroxide and the fraction coming over at 140–160° C. collected. This consists of styrolene (recognised by its smell) if phenylethyl alcohol was originally present. Its presence is confirmed by forming the dibromo derivative, which melts at 72° C. The accidental presence of geraniol or rhodinol does not interfere unless they are present in great excess. The reaction

is particularly useful in perfumery practice in dealing with synthetic alcohols of closely approximating b.pt.s., and the quantity of dibromostyrolene formed affords a rough indication of the proportion of phenylethyl alcohol originally present.

D. G. H.

Cresyl Esters of Phenyl-Acetic Acid. L. C. Raiford and J. G. Hildebrand. (*Amer. J. Pharm.*, 1929, 101, 481-484.)—The *p*-cresyl ester of phenylacetic acid is included as a synthetic perfumery compound in the list of the U.S.A. Tariff Commission, but few data as to its properties are available. The isomeric cresyl esters of phenylacetic acid may be prepared by the action of phenyl acetyl chloride on the cresols. The chloride is made by heating 1 part of phenyl acetic acid and 1.5 to 2 parts of thionyl chloride for 3 hours at 80–100° C. in a flask fitted with a thermometer and with a connecting tube high enough (40 cm.) to prevent thionyl chloride passing over, and with another thermometer at its bend. The excess of thionyl chloride is distilled off under atmospheric pressure, and the residue fractionated under reduced pressure. At 100–101° C. with 16 mm. pressure 92 per cent. of phenylacetyl chloride was obtained as a colourless heavy liquid. Sixteen grms. of the chloride mixed with 11 grms. of freshly distilled *para*-cresol, heated at 90° C. until evolution of hydrochloric acid ceases, cooled, and poured into 200 c.c. of chilled 6 *N* sodium hydroxide solution yielded 83 per cent. of solid *p*-cresyl phenyl acetate in small blocks of m.pt. 74–75° C. This differs from the m.pt. given by Poucher, *viz.* 86° C. (*Perfumes, Cosmetics and Soaps*, Vol. I, p. 97). The *meta* salt was obtained as colourless plates with a yield of 72 per cent., and had a m.pt. of 51–52° C. and the *ortho* salt (yield 82 per cent. of colourless plates) had a m.pt. of 44–45° C.

D. G. H.

Volumetric Determination of Sulphur in Crude Petroleum. G. Woodward. (*Ind. Eng. Chem., Anal. Edit.*, 1929, 1, 117–118.)—A quantity of the petroleum, sufficient to produce from 0.03 to 0.25 grm. of sulphuric acid, is burned in an oxygen bomb, the contents of which are then dissolved in a small quantity of water, 0.2 c.c. of concentrated potassium iodide solution is added, and any yellow colour due to the liberation of iodine by ferric salts is destroyed by heating the solution after adding a small quantity of aluminium powder. After cooling, alcohol is added in amount sufficient to make the alcoholic strength of the solution 50 to 70 per cent., and the sulphuric acid is titrated with standardised lead nitrate solution. The end-point of the titration is sharp, since in a 50 to 70 per cent. alcoholic solution yellow lead iodide does not form until all lead sulphate has been precipitated.

W. P. S.

Electrostatic Method for the Determination of Fusain in Bituminous Coal. J. D. Davis and J. A. Younkens. (*Ind. Eng. Chem., Anal. Edit.*, 1929, 1, 165–167.)—The coal is ground to pass a 60-mesh sieve, and 0.5 grm. of the sample is submitted to centrifugal action with a mixture of light petroleum and carbon tetrachloride (sp. gr. 1.40–1.45). This treatment floats most of the coal, which is removed, and the mass of fusain, etc., at the bottom of the centrifuge tube is trans-

ferred to a watch-glass and dried. The dried residue is then spread on the bottom plate of an electrostatic separator. This consists of a glass case; the bottom electrode is an aluminium tray, and the top electrode is a sheet of lead foil glued to the glass. The whole case is mounted so that it may be shaken automatically and slowly. When a high tension current is passed between the electrodes the fusain is attracted and repelled alternately; the motion of the particles is rapid, and if a current of dry inert gas is passed through the case, the fusain may be removed from the field and collected. The coal and foreign substances remain on the bottom electrode. The separated fusain should be examined microscopically to ascertain whether a further treatment is necessary to remove any adhering coal particles.

W. P. S.

Inorganic Analysis.

Quantitative Determination of Neon in Natural Gases. N. P. Péntcheff. (*Compt. rend.*, 1929, 189, 322–324.)—Argon, krypton and xenon are adsorbed on coconut charcoal at the temperature of liquid air from the mixture of rare gases (obtained after removal of the common gases by the usual methods), and their absence confirmed by spectral analysis. The density of the residual helium-neon mixture is then determined. The method was tested on mixtures in known proportions of the above rare gases, and the results obtained for a natural gas from a Bulgarian spring were shown to confirm Moureu and Lepape's astrophysical theory.

J. G.

New Method for the Separation of Lead and Bismuth. Frick and Engemann. (*Chem. Zeit.*, 1929, 53, 601–602.)—The method is suitable for the determination of bismuth in metallic lead, and obviates the previous precipitation of lead as sulphate. The nitrate solution (300 c.c.) is treated with 3 to 5 drops of Congo red solution (1.5 per cent.), the blue flocculent precipitate of the dye assisting in the subsequent precipitation. Neutralisation to a blue-red tint is effected with sodium hydroxide. The solution is stirred and treated with 0.7 per cent. cinchonine hydrochloride solution. The precipitate is filtered off after half an hour; a few drops of filtrate are tested with potassium iodide solution for complete precipitation of bismuth (traces of bismuth suffice to impart a brown tint to the lead iodide precipitate). If bismuth is indicated, the neutralisation has not been pushed far enough, and the filtrate must be re-treated after suitable addition of alkali. The precipitate is washed free from lead with cold water containing 10 c.c. of cinchonine solution per litre and neutralised to blue-red by addition of a little Congo red and dilute nitric acid. Filter and precipitate are boiled with 100 c.c. of water and 20 c.c. of nitric acid. The pulped paper is removed by filtration, the filtrate evaporated with 20 c.c. of sulphuric acid until white fumes are freely given off, and the bismuth determined by the usual colorimetric iodide method. The precipitation by the cinchonine salt appears to be a hydrolytic one. Accurate results are claimed.

W. R. S.

Rapid Determination of Mercury and Cadmium. G. Spacu and G. Suciu. (*Z. anal. Chem.*, 1929, 77, 334–343.)—*Mercury.* The neutral or faintly ammoniacal solution (80 to 500 c.c.) is treated with an excess of potassium iodide and, near the boiling-point, with a boiling concentrated solution of copper diethylenediamine nitrate, $\text{Cu}[\text{C}_2\text{H}_4(\text{NH}_2)_2]_2(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ in excess. On cooling, tabular deep blue-violet crystals separate. They are collected on a porous porcelain crucible, washed with a solution containing 0.1 per cent. each of potassium iodide and of the precipitant, with alcohol, and finally with ether, and weighed after 5 to 10 minutes' drying *in vacuo*. The precipitate has the composition $(\text{HgI}_4)\text{Cu}[\text{C}_2\text{H}_4(\text{NH}_2)_2]_2$, and contains 22.49 per cent. Hg. The method is applicable in presence of ammonium chloride and nitrate; hence an *aqua regia* solution can be submitted to the process after neutralisation with ammonia. The reagent may be prepared by treatment of a copper sulphate solution with one of ethylenediamine until the characteristic deep blue colour is produced; an excess of the base is not harmful. *Cadmium.*—The neutral solution containing an excess of potassium iodide is boiled and treated exactly as described under Mercury, except that the precipitate is washed with a solution containing one per cent. of potassium iodide and 0.3 of the precipitant, followed by alcohol and ether. The precipitate has the same constitution as the mercury compound and contains 13.99 per cent. Cd. The precipitant must not, in this case, contain free ethylenediamine, nor should ammonium salts be present. The determination is stated to be less advantageous than that of mercury. W. R. S.

Determination of Small Quantities of Copper with 5, 7-Dibromo-o-Oxyquinoline. L. W. Haase. (*Z. anal. Chem.*, 1929, 78, 113–124.)—The method is designed for the rapid determination of copper (0.5 to 10 mgrms. per litre) in industrial water, sewage, etc. A 0.5 per cent. solution of the base in 5 *N* hydrochloric acid is used. Two hundred c.c. of the sample are treated in the cold with a moderate excess of the reagent, and the precipitate coagulated by 20 minutes' digestion on the water-bath. The precipitate is dried at 105° C. for an hour, then heated for 2 to 3 hours at 150° C. for the volatilisation of the excess of precipitant, and weighed. The acidity of the liquid to be tested should not exceed 0.2 *N*; at 0.5 *N* concentration, the small quantity of copper fails to precipitate. Alkaline waters are acidified (methyl orange). Acetic acid and alkali salts do not interfere. Organic colloids, humic acid, etc., in sewage are first destroyed by treatment of the water with one c.c. of *N* hydrochloric acid and 10 drops of perhydrol, and gentle boiling till the liquid is colourless. Any precipitate thus produced is filtered off, previous to the precipitation of the copper. W. R. S.

Accuracy of the Gutzeit Method for Arsenic. J. R. Neller. (*J. Assoc. Off. Agric. Chem.*, 1929, 12, 332–341.)—A study has been made of the accuracy of the method for aliquot portions of lead arsenate solutions obtained by dipping sprayed apples in 10 per cent. hydrochloric acid. The average probable percentage error of the mean of all the possible pairs obtainable in a number of groups of 8 to 11 determinations each was 6.6 per cent., and this represents the normal

limit of accuracy of the method. The results were independent of temperature between 18° and 33° C., and were the same whether the stannous chloride was added before or after the solution was heated with potassium iodide. In the presence of sulphuric acid, however, the stannous chloride should be added when the solution is finally cooled, so as to avoid formation of sulphur dioxide. Hydrochloric acid is preferable to sulphuric acid, which may produce hydrogen sulphide, and the reduction of arsenate to arsenite should be carried out in 10 per cent. acid solution at 80° C. for 10 minutes. J. G.

Preparation of Antimony-Free Arsenious Oxide and Determination of Minute Amounts of Antimony in Arsenious Oxide. C. W. Foulk and P. G. Horton. (*J. Amer. Chem. Soc.*, 1929, 51, 2416-2419.)—In the preparation of arsenious oxide of a high degree of purity, antimonious oxide is by far the most troublesome of the impurities to remove. A rapid and simple method for the preparation of antimony-free arsenious oxide is now described, and also an application of this method to the qualitative detection and rough quantitative determination of minute amounts of antimony in arsenious oxide. Briefly stated, the new method consists in the conversion of the arsenious oxide into arsenious chloride, by distillation of the oxide in concentrated hydrochloric acid in a current of hydrogen chloride gas; this is then followed by removal of the antimony by repeated shaking out of the chloride in a separating funnel with concentrated hydrochloric acid. The antimonious chloride is so much more soluble in concentrated hydrochloric acid than is arsenious chloride that shaking out with only a few portions of acid will completely remove a considerable amount of it. The lower layer is drawn off and the process repeated until the acid layer shows no antimony *vide infra*. Hydrolysis of the arsenious chloride to give arsenious oxide again is accomplished by allowing the chloride to run slowly from a separating funnel into a large beaker of boiling water with vigorous stirring. On cooling, arsenious oxide separates as a fine white solid which is filtered, washed free from acid, and further purified by recrystallisation and sublimation. The acid layer is tested for antimony as follows:—The layer is heated in the distillation apparatus as long as any oily arsenious chloride which it holds in solution distils over. The residue is then transferred to a beaker and treated, while still hot, with hydrogen sulphide. All the arsenic remaining is precipitated as yellow arsenious sulphide, antimony being left in solution. The precipitate is filtered off on a double filter paper, and the filtrate diluted with three times its volume of water, and again saturated with hydrogen sulphide, when antimony, if present, comes down as orange antimonious sulphide. To detect very minute amounts of antimony, the solution should be left to stand for a day or two, for an orange-coloured turbidity may become a distinct precipitate. Less than 0.001 per cent. can be detected by this test. Fairly good quantitative determinations can be made by comparing the precipitated sulphide with a series of similarly prepared precipitates of known amounts of antimony. If only a trace of antimony is suspected in the case of arsenious oxide, the residual acid solution in the distillation flask, after separation of the arsenious chloride, is examined for antimony. P. H. P.

Permanganate Titration of Antimony in White Metal. A. Wassilieff and H. Stutzer. (*Z. anal. Chem.*, 1929, **78**, 97-102.)—When sulphuric acid is used for the solution of the sample and the acid diluted with water and hydrochloric acid previous to permanganate titration, a small amount of antimony is adsorbed by the lead sulphate, and escapes titration. The following procedure is recommended: 1 grm. is boiled with 15 c.c. of strong sulphuric acid until sulphur dioxide is completely expelled. After cooling, 50 c.c. of water, 10 c.c. of strong hydrochloric acid, and again 150 c.c. of water are added. The solution is titrated at 15° C. with 0.1 N permanganate till the pink end-point persists for one minute during agitation. The flask is inclined to allow the precipitate to settle; the liquid is cautiously decanted, and the precipitate dissolved by warming with 20 c.c. of hydrochloric acid and 10 of water. The solution obtained is transferred to a 500 c.c. flask, diluted with 400 c.c. of water, and the titration concluded at 15° C. In a series of tests, 1.56 to 3.34 per cent. of the antimony content was found in the lead sulphate.

W. R. S.

Colorimetric Method for the Micro Analysis of Cobalt. L. Michaelis and S. Yamaguchi. (*J. Biol. Chem.*, 1929, **83**, 367-373.)—It is ascertained by a colorimetric method that the oxidised cobalt complex of cysteine contains cobalt and cysteine in the ratio of 1:3. This fact in combination with the amount of oxygen necessary to obtain this complex from its constituents suggests as formula for the oxidised cobalt complex of cysteine: $\text{Co}(\text{SCH}_2\text{NH}_2\text{CH}(\text{COO})_3\text{H}_2$. A sensitive and accurate method is described for the micro analysis of cobalt which is based on the formation of this complex. The procedure is as follows:—The cobalt compound to be analysed, in such an amount as to contain no more than 5 mgrms. of cobalt, is heated in a platinum crucible with about 1.5 c.c. of concentrated sulphuric acid. The platinum crucible is placed in a larger nickel crucible and heated to dryness. After cooling, 25 c.c. of phosphate buffer (Sørensen) pH 7.5 and cysteine hydrochloride crystals in excess (*i.e.* about 10 mgrms.) are added, and the oxidation of the cobalt complex is accomplished by the gentle shaking of this solution in a beaker so as to expose it to the air. Oxidation is complete in a minute or so, and the brown colour is stable over many hours or longer. It is then compared in a colorimeter with a solution freshly prepared in the same way from a known amount of cobalt sulphate ($\text{CoSO}_4 + 7\text{H}_2\text{O}$ crystals free from nickel and iron), which need not be heated with sulphuric acid. Analyses of known amounts of cobalt in range from a fraction of 1 mgrm. up to 5 mgrms. were correct within at least ± 5 per cent. The volume of the solutions may be smaller, if necessary, and $\frac{1}{10}$ mgrm. of cobalt can be determined with the same accuracy. The presence of iron, copper or manganese does not interfere with this method. Nickel can just be detected by a slight change of colour when the ratio of cobalt:nickel=1:2; it is not likely to be present in so large an excess in tissues. The fact that, in general, the removal of nickel is unnecessary imparts a considerable advantage to this method compared with the method applied by Bertrand and Macheboeuf.

P. H. P.

Determination of Chromium Oxide (CrO_3) in Lead Paints. E. J. Davis. (*Chemist Analyst*, 1929, 18, [iii], 8.)—The oxide is extracted from 1 grm. of the vehicle-free pigment in 50 c.c. of a boiling 16 per cent. solution of potassium hydroxide, the diluted solution filtered, and the residue well washed. The extract (400 c.c.) is neutralised at 60°C . with glacial acetic acid, and 15 c.c. added in excess to precipitate lead chromate, while lead sulphate is retained in solution. After 30 minutes the former is filtered off in a Gooch crucible, washed, dried and weighed. In the presence of zinc chromate 2 grms. of lead chloride are added before the addition of the acetic acid. Prussian blue and other pigments do not interfere, and an accuracy of ± 0.1 per cent. is obtainable. J. G.

Volumetric Determination of Sulphur in Polysulphides. P. Szeberényi. (*Z. anal. Chem.*, 1929, 78, 36–40.)—The polysulphide solution is boiled with a known excess of 0.1 *N* sodium sulphite solution: the conversion to thiosulphate is complete after 2 to 3 minutes, the liquor becoming colourless. After cooling, the solution is titrated with 0.1 *N* iodine. The conversion of polysulphide into monosulphide does not bring about any change in the iodine consumption; that of sulphite into thiosulphate, on the other hand, reduces the iodine consumption to one-half. Another portion of liquor is titrated direct with 0.1 *N* iodine: this volume is added to that equivalent to the 0.1 *N* sulphite solution, and the iodine consumption of the sulphite-treated portion subtracted from the above sum. The difference, multiplied by 0.0032, gives the quantity of polysulphide sulphur proper (*i.e.* sulphur in excess of monosulphide sulphur). The thiosulphate invariably present in polysulphide liquors does not affect the accuracy of the determination. W. R. S.

Analysis of Insecticides containing Fluorine Compounds. L. Hart. (*Ind. Eng. Chem., Anal. Edit.*, 1929, 1, 133–135.)—*Mixtures of alkali silicofluorides and boric acid.*—The silicofluoride is precipitated as its potassium salt in the presence of alcohol (1:2), and, without removing the precipitate, the boric acid remaining in solution is titrated in the usual way. The total acidity is titrated in another portion of the sample, and the difference between this and the acidity due to boric acid is a measure of the alkali silicofluoride. One c.c. of 0.2 *N* sodium hydroxide solution is equivalent to 0.0094 grm. of sodium silicofluoride. *Preparations containing soluble fluorides and arsenic compounds.*—The arsenic is oxidised by hydrogen peroxide and precipitated as silver arsenate from acetic acid solution in the presence of sodium acetate. After filtration the arsenic and fluorine may be determined in the precipitate and filtrate, respectively, by the usual methods. *Mixtures of sodium fluoride, sodium bifluoride and sodium silicofluoride.*—The total acidity of the sample, due to bifluoride and silicofluoride, is determined, phenolphthalein being used as indicator; the titration should be carried out in a platinum vessel and while the solution is boiling. The neutral solution is diluted to 200 c.c., and an aliquot portion used for the determination of total fluorine. To determine the bifluoride, 0.5 grm. of the sample is treated in a platinum basin with 1 grm. of potassium chloride, 25 c.c. of water and 25 c.c. of alcohol.

The mixture is cooled to 0° C., and kept at this temperature while the acidity due to bifluoride is titrated. The difference between this titration and the total acidity gives the amount of the silicofluoride. The fluorine equivalent of bifluoride and silicofluoride deducted from the total fluorine gives the quantity of fluorine present as fluoride.

W. P. S.

Physical Methods, Apparatus, etc.

Photo-Chemical Methods of Testing Sources of Ultra-Violet Radiation.

F. C. Hymas. (*Quarterly J. Pharm.*, 1929, 2, 281-291.)—In McKenzie and King's method (*Practical Ultra-Violet Therapy*) 2 c.c. of carbon tetrachloride are exposed for 10 minutes in a quartz tube at a distance of 17.5 cm. from the source of radiation, and the chlorine (liberated according to the equation $2\text{CCl}_4 = \text{C}_2\text{Cl}_6 + \text{Cl}_2$) is determined by titration with sodium thiosulphate in the presence of potassium iodide. Since the reaction occurs principally in the vapour phase, the method is not recommended, as the test is susceptible to temperature variations, and the reagent and reaction products cannot be accurately transferred to and from the tube. Anderson and Robinson (*J. Amer. Chem. Soc.*, 1925, 47, 718) expose, under the same conditions, 2 c.c. of a solution containing 6.3 grms. of oxalic acid and 4.27 grms. of uranyl sulphate per litre and titrate the products of catalytic decomposition of the former (carbon dioxide and formic acid) with 0.02 N potassium permanganate solution in the presence of sulphuric acid. The present authors measure in terms of the Lovibond scale the blue colour produced from a 0.1 N solution of potassium iodide containing 0.1 per cent. of dissolved starch. It is shown that the last two methods give accurate results for the first 20 minutes of exposure, the temperature coefficients per 10° C. being 1.035 (between 25° and 45° C.) and 1.042 (between 25° and 62° C.), respectively. Discrepancies in comparative results are due to the fact that a layer 2.5 cm. thick of the oxalic acid and uranyl salt solution effects complete extinction below 3600 Å. and partial absorption to 4100 Å., whilst potassium iodide and starch solution absorbs all rays below 2625 Å. completely, and partially to 3500 Å. The author's method showed that the emission from 6 lamps fell rapidly during the first 1000 hours of use to a low constant value, corresponding, presumably, with the absorption band of the decomposed silica.

J. G.

Reviews.

INDUSTRIAL CARBON. By C. L. MANTELL, Ph.D. Pp. x+410. With 89 Text Figures. New York: D. Van Nostrand Company, Inc.; London: Chapman & Hall. 1929. Price 21s. net.

This is one of a number of Industrial Chemical Monographs which have been planned under the joint editorship of Drs. W. Lee Lewis and Harrison E. Howe. The present one deals solely with carbon and its industrial applications, and the

appearance of the book affords evidence not only of the importance of carbon in the many and diverse forms in which it finds application in industry, but also of the increasing specialisation which is such a striking feature of present-day chemical industry. There was need for a book of this character, if only for the purpose of bringing within one volume the increasing amount of information relating to carbon and its uses—information hitherto found widely scattered amongst the pages of many scientific papers, technical journals and patent specifications. It is to be questioned, however, whether the present volume is sufficiently abreast of the times and as critical as might be wished for one to be able to accord its author unstinted praise.

On the first page one reads: "Due to its dirty habits and uncultured nature, carbon has often been in the step-child's position; as a result of its black, grimy outward appearance and its shy habits but very little attention has been paid to it in the literature." This is the language of the films; other passages in similar vein in the earlier pages are indicative of the somewhat popular manner in which the book is written. One is disposed to disagree with the view that "but very little attention has been paid to it in the literature." In the reviewer's opinion, a great deal of information respecting carbon has found its entry into technical literature in recent years, and it is charitable to assume that, owing to the author's "shy habits," he has failed to notice or appreciate some of this, for otherwise the omissions are difficult to understand.

There are twenty-nine chapters in the present volume, many of them very short and containing but a few pages in all. The subject-matter embraces the study of graphite (both natural and artificial), carbon black and other black pigments, charcoal considered as a fuel, the various decolorising and adsorbent charcoals, carbon electrodes, carbons for arc-lights and other special purposes, battery and welding carbons, and carbon refractories. The treatment embraces, in addition, the applications of these various materials in the arts and manufactures. Throughout the book there are copious references to original scientific and technical publications and research and patent specifications, mainly of United States origin. But there are a number of important omissions in this respect, and, as few of the references bear a later date than 1923, the present volume is not as up-to-date as the reader has a right to expect.

The chapters dealing with graphite are quite good and leave nothing to be desired. In regard to carbon black too little notice has been accorded the subject of thermal decomposition; this is a field of investigation in which much work has been recorded in recent years. The influence of the temperature of formation has likewise been shown to have a considerable bearing on the physical properties of the resulting carbon; but most of these recent advances find no mention in the present volume. Likewise, the author's treatment of the subject of carbon black in compounded rubber is much too scanty, especially in view of the fact that the rubber industry is by far the largest user of the pigment.

In the chapters dealing with carbonaceous ink pigments and black paint pigments, there is little record of research of the past few years. The reviewer was responsible for a modest volume, "Blacks and Pitches," which appeared in 1925. It is curious to note many points of resemblance between this earlier volume and Dr. Mantell's. The concluding paragraph (7 lines) on p. 91 is almost identical with the third paragraph on p. 61 of the reviewer's book; the third paragraph (12 lines) on p. 94 of Dr. Mantell's book is identical, even to the extent of punctuation marks, with the second paragraph on p. 63 of the reviewer's book, whilst Table IV on p. 95 of the former is Table XV on p. 63 of the latter; even an error in copying in the latter appears in the former. Furthermore, the table and the concluding paragraph but one on p. 117 of the former book are, respectively, Table XII and last paragraph on p. 49 of "Blacks and Pitches." A numerical error in the last-named paragraph appears also in the corresponding paragraph of the former book. That two authors, unknown to each other, with an interval of four years between their efforts, and with the width of the Atlantic Ocean between them, should choose the same form of words in several paragraphs, and out of the mass of data available should each separately select in several tables identical particulars (with like errors in copying) is but another of those striking coincidences which from time to time break the monotony of life. Who shall have the temerity to deny that truth is indeed stranger than fiction?

The several chapters dealing with charcoal and decolorising carbons contain much useful information, though many recent researches in this connection appear to have escaped the author's attention. The short section dealing with the recovery of gasoline from natural gas is rather disappointing, particularly as coming from an American author, in view of the industrial importance of the subject. An important paper last year by Edeleanu, jun., on the application of this method in Roumania receives no mention in the volume under review.

The chapters devoted to carbon electrodes and allied manufactures are very detailed and appear well done, though there is an undoubted American bias in the treatment accorded. In Chapter XXIX the author has enumerated the chemical and physical properties of carbon, the references (to the total of 48) to the original sources of the data being given in each case. This tabulation will be found exceedingly useful.

The illustrations are good, though several of them are of plant now somewhat antiquated. The general style of the book is good, and the indexing has been carefully done. Should the author be called upon at a later date for a new edition it would be advisable that he should make himself familiar with the Journal of the Oil & Colour Chemists Association, with the Annual Reports on the Progress of Applied Chemistry, published by the Society of Chemical Industry, and with Chemical Abstracts in his own country. He will then be better able to give his readers up-to-date references to all recent work in the field he has chosen to describe.

H. M. LANGTON.

CHEMISTRY IN THE HOME. By J. B. FIRTH. First Edition. Pp. 246, with 17 illustrations. London: Constable & Co., Ltd. 1929. Price 5s. net.

This volume is an elementary text-book on hygiene, and is intended for the use of housewives, welfare workers and the teachers in girls' schools who have little or no knowledge of chemistry. It is divided into two parts, the first dealing with water, fuels, ventilation, lighting and other general subjects, whilst the second is devoted to foods and beverages.

To produce a volume of this nature for the use of the layman is by no means a simple matter, for, in addition to his natural difficulty in understanding a new subject, the reader is liable to misinterpret statements of fact and to arrive at false conclusions. The author has done his work in this respect very successfully, and, in spite of the wealth of material compressed into a small volume, his conciseness and freedom from ambiguity should prevent such consequences.

The author has devoted considerable industry to the compilation of the text, but has in some cases exceeded the limits of the title, for the formation of stalactites, lacustrine or oceanic salt deposits, and the manufacture of coal gas hardly come within the domain of home chemistry. Unfortunately many minor shortcomings are present which should have been corrected, and among the examples of bad grammar we find "This group of gases *are* known as the rare gases" (p. 14); and "the water can only retain the dissolved rock so long as *they keep* the carbon dioxide" (p. 35). Further, mis-spelt words are too frequent and include "epithe-leum," "carbohdyrates," "Lilum" (of a starch grain), "pellogra," and others. Such faults would in some cases be detected and corrected by the readers, but the following incorrect statements of fact are likely to be accepted as true: "When nitrocellulose is dissolved in *ether*, it yields collodion" (p. 152); "Spermaceti, *an oil* obtained from the sperm whale" (p. 80); "Lysol contains cresol, castor oil and potassium hydroxide" (p. 116); "Apple *protein* is now a commercial article" (p. 191), and so on.

Apart from these errors, the volume contains much of general utility, but the material provided requires considerable dilution if the readers are to escape mental dyspepsia and the satiety induced by the acquisition of that little knowledge which so often proves dangerous. The illustrations are, on the whole, good and clear, but in Fig. 4 the vertical limbs of a syphon barometer are, in proportion, separated by a distance of a foot, and more interest would have been added to the micro-drawings of textile fibres, starches and yeast had the magnifications been given. The bacterial plate culture depicted in the frontispiece also requires fuller explanation. The page references in the text, numerical data and index are accurate; but the index, although containing over 360 items, is not sufficient to include the many varied matters dealt with in the book. In spite of its blemishes, the volume is far from being a failure, and the author has done well in producing a work of considerable interest and utilitarian value to those for whom it is intended, but a second edition should be submitted to decidedly more careful reading of the proofs.

T. J. WARD.

CHEMISTRY OF PULP AND PAPER-MAKING. By EDWIN SUTERMEISTER, S.B.
Second edition. Pp. x+565. New York: John Wiley & Sons, Inc.;
London: Chapman & Hall, Ltd. 1929. Price 32s. 6d. net.

The second edition of this publication will be welcomed by all connected with the industry of pulp and paper-making. The name of Sutermeister in itself commands respect. The book, re-written in the light of knowledge gained since 1920 (date of first edition), only increases that respect. Lucidity, thoroughness, and a critical broad-mindedness are its characteristics.

A concise but comprehensive survey of cellulose, the basic raw material of the industry, a compound the constitution of which is still problematical, makes Chapter I a valuable guide to the seeker after up-to-date information on this substance and its reactions.

Under "Fibrous Raw Materials," an account is given of the vegetable cell, together with morphological, microscopical and other data for all the well-known paper-making fibres, including pulps from various woods. This section is admirably illustrated by photo-micrographs made for the Bureau of Standards.

The descriptions of the soda, sulphate, sulphite and mechanical processes for the preparation of wood pulps are supplemented by a very interesting chapter on the newer methods, *e.g.* the "Keebra," "Ramar," and "Explosion" processes. Another modern development described is the bleaching of pulp by liquid chlorine, and up-to-date methods for the evaluation of wood pulp for strength and beating properties are critically examined.

Regarding the vexed question of sizing paper, Sutermeister indicates that little help is to be obtained from a control of the P_H value of stock. His work suggests that the solution lies in drying and its effects; at the same time his attitude is by no means dogmatic. Sizing with such comparatively novel substances as sodium silicate and rubber latex is discussed; the claims originally made for the latter are shown to be much exaggerated, a fact in accordance with the reviewer's experience. Loading and filling materials are dealt with very fully, and the photo-micrographs in illustration should prove helpful to any analyst endeavouring to determine the type of filling present in a sample of paper. A simple apparatus for the determination of grit in fillers, by flotation, is described; this is a welcome alternative to the complicated elutriation usually recommended.

The colouring of paper with both inorganic pigments and organic dyes is usefully surveyed, and methods of determining the fastness of dyes to chemicals with which they come in contact, as well as some suggestions on the testing for fastness to light, are included. In discussing coated papers much valuable information is recorded on the testing and control of the materials used, *e.g.* glue, casein and other adhesives, blanc fixe, satin white, etc.

As regards the testing of paper, Sutermeister has adopted the methods of the Technical Association of the Pulp and Paper Industry. He gives only the essential

methods, however, and these in synopsis. While they are sufficiently full to meet the needs of routine work in a paper mill, the general analyst may desire a wider treatment. The references, however, do much to supply this minor deficiency.

In dealing with printing, the author points out defects giving rise to "complaints," and the possible faults of printer, paper-maker, and ink-maker, are enumerated. Anyone having to advise on printer's troubles should find this section helpful.

The appendix contains some useful physical data and conversion tables. The amount of data and the number of analytical methods included in the text, constitute distinctive features of this well-written and well-illustrated book.

WILLIAM DICKSON.

SHAKSPEARE FORGERIES IN THE REVELS ACCOUNTS. By S. A. TANNENBAUM, M.D.
Pp. 89, with 22 full-page facsimiles. New York: Columbia Press; London:
Oxford University Press. Price 75s. net.

In these days of cheap mass-production of books it is a pleasure to meet with one so luxuriously produced as this volume. It is printed on good thick paper in bold clear type, and, although large, is easy to open and to hold, and the facsimiles of the original documents are admirably reproduced. The author, too, gains much by having his argument, which demands the closest attention, clothed in a form which attracts instead of repelling the reader.

The book deals with a controversy which is now more than sixty years old, but which, as the author shows, is still not closed. The story opens in 1842 with the alleged discovery in a cellar of Somerset House of the official books of the Revels Accounts for the years 1604-5 and 1611-12, by Peter Cunningham, a clerk in the Audit Office. As these accounts fix the date of some of Shakespeare's plays, they were at once accepted as a most valuable discovery, and a full transcript of them was published. Little more was heard of them until 1868, when Cunningham, who had by that time fallen a victim to drink, offered to sell them to the British Museum, but Sir F. Madden, the Keeper of the MSS. Department, claimed that the documents were already the property of the nation, and established the claim.

As soon as they were open to inspection doubts as to their being genuine were expressed, and positive opinions were put forward on each side. The controversy, an outline of which is given in this book, culminated in 1911, when Mr. Ernest Law obtained opinions on the writing from some of the leading palaeographers of the day, including Sir George Warner. As doubts had previously been expressed concerning the ink, Sir James Dobbie (then Government Chemist) was asked to apply chemical tests and to report upon it. Apparently it was tacitly accepted that only the lists of plays produced were open to suspicion, and that the rest of the documents was unquestionably ancient.

Dobbie's report, which is given here in full, was to the effect that his microscopical and chemical examination of the book of 1604-5 revealed no differences between the inks in any part of the document, and that there was no indication that the ink in one part had faded more than that in another, as was to be expected if part of the writing was 200 years old, whilst another portion had been written in or about 1868, as suggested.

This is probably the first instance where a chemist has been asked to assist in solving a literary problem, and the report has thus a special interest. The conclusions embodied in it are relative only, but Mr. Law has made use of it to support his view in a way which the report itself does not warrant. Thus he says that the ink has been demonstrated not to be modern in chemical constitution, and that it has been shown to be "absolutely ancient." Such distortions of the report of a chemist are not unknown in the fields of advertisement, but should not be brought into a literary and scientific controversy.

Largely owing to the stress laid upon this report and to the opinions of the palaeographers, the authenticity of these documents has now been generally accepted, although some faint voices of doubt have been heard.

In the present work, however, Dr. Tannenbaum brings many cogent arguments, illustrated by photographic reproductions, to prove that, after all, the Revels Accounts are forgeries. He condemns the opinions of the palaeographers on the ground that they had not the training to analyse variations in writing, and that they did not use the microscope, which would have shown the variations.

With regard to the chemical report, Dr. Tannenbaum asserts that the entire documents are forgeries, and that because the same kind of ink was used in different portions of a document, and apparently at the same time, it does not follow that the ink was ancient. Apart from that, he claims that some of the so-called "alterations," when examined under the microscope, show indications of having been made over original outlines, and that they are fraudulent emendations, not legitimate alterations.

It will thus be seen that several interesting scientific problems connected with these documents demand further work before they can be regarded as settled, but the author has undoubtedly made out a very strong case in support of his view, and his book will repay careful study by those who are even indirectly interested in his subject.

EDITOR.



THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, October 2nd, the President, Mr. Edward Hinks, being in the chair.

Certificates were read for the first time in favour of:—Alfred George West, A.I.C., William Rhys Davies, F.I.C., Ernest Roadley Dovey, A.R.C.Sc., F.I.C., James Gray, F.I.C., James Henderson, B.Sc., A.I.C., Claude Alexander Scarlett, B.Sc., A.K.C., A.I.C., Percy Arthur William Self, B.Sc., F.I.C., Thomas Brooks Smith, B.Sc., A.R.C.S.

Certificates were read for the second time in favour of:—John William Haigh Johnson, M.Sc., F.I.C., Mamie Olliver, B.Sc., A.I.C., and George Edward Shaw, B.Sc.

The following were elected Members of the Society:—Alfred Norman Leather, B.Sc., F.I.C., Richard Harold Morgan, B.Sc., A.I.C., and William George Painton, B.Sc., A.I.C.

The following papers were read and discussed:—"Chemical Tests in Relation to Fur Dermatitis," by H. E. Cox, M.Sc., Ph.D., F.I.C.; "A Nomogram for use in Gas Analysis," by J. H. Coste, F.I.C.; "The Composition of Irish Winter Butter," by P. S. Arup, A.C.G.I., M.Sc., F.I.C.; and "Investigations into the Analytical Chemistry of Tantalum, Niobium and their Mineral Associates: XVI. Observations on Tartaric Hydrolysis; XVII. The Quantitative Precipitation of the Earth Acids and certain other Oxides from Tartrate Solution," by W. R. Schoeller, Ph.D., and H. W. Webb.

NORTH OF ENGLAND SECTION.

A MEETING of the Section was held at Manchester on October 19th. The Chairman (Mr. S. E. Melling) presided, and there were present the President (Mr. E. Hinks) and 28 Members.

Messrs. H. M. Mason, M.Sc., F.I.C., and A. R. Tankard, F.I.C., opened a discussion on "Quality in Relation to Foodstuffs." A most interesting debate followed, in which the following took part:—The President, Prof. W. H. Roberts, Messrs. J. Evans, E. M. Hawkins, C. J. H. Stock, G. D. Elsdon, and J. Hanley. A communication on the subject was read from Dr. J. T. Dunn.

Meniscus Corrections involved in the Calibration of Graduated Tubes.

BY A. MORE, F.I.C.

It is impossible to conduct the calibration of some forms of apparatus used in gas analysis, such as closed tubes, in the position in which they are used. The usual method employed is to determine the volume of water or mercury required to fill the tubes in the inverted position until the horizontal plane tangential to the meniscus corresponds with the graduated marks, and then to deduct, when water is used, or add, when mercury is used, the so-called "meniscus error" to compensate for the reversed direction of the meniscus curve with reference to the graduation marks in the two positions. When the same liquid is used in the calibration of, and in the measurements with, gas vessels, the meniscus error is double the meniscus correction, which is the volume in the tube between the horizontal plane tangential to the meniscus and the surface of the water or mercury, as the case may be.

A similar problem arises in the calibration of small tubes designed to measure the volume of insoluble or extraneous matter collected by sedimentation or centrifugal separation from certain liquid media. The deposits obtained by sedimentation have, and those obtained on centrifuging can (with suitable manipulation) be arranged to have a horizontal upper surface. The tubes can be calibrated conveniently by weighing them empty and with liquids adjusted to the graduated marks; but, in this case, the difference between the volumes of the sediment and of the liquid filled to the same mark amounts to a single meniscus correction.

It is found, however, that the values of the double meniscus correction, given in different text-books dealing with the calibration of gas burettes for both water and mercury, differ materially. Treadwell and Hall's *Quantitative Analysis* (1928, p. 639) gives one series of values, supplied by W. Schloesser, and *Sutton's Volumetric Analysis* (1924, p. 519) gives another, the former agreeing with values given in Kurt Arndt, *Handbuch der Physikalisch-Chemischen Technik*, and the

latter with the values obtained by H. Göckel, quoted in Landolt and Börnstein's *Physikalisch-Chemische Tabellen*, 3rd edn., p. 29.

Göckel's data (*Z. angew. Chem.*, 1903, 16, 49) were published to controvert a statement by Winkler that the original values given by Bunsen (*Gasometrische Methoden*, 1877, p. 37) were too high, and as Göckel's results were in fair agreement with Bunsen's, they have been accepted, as stated above, in preference to the results obtained, using a different method of measurement, and published later, by Winkler (*Z. angew. Chem.*, 1903, 16, 372.)

The *International Critical Tables* (Vol. I, p. 72) give data from which the meniscus correction can be calculated for mercury in tubes of known diameter and with varying heights of meniscus. For any given diameter of tube the meniscus correction with a flat meniscus may be only one-tenth of the correction when the meniscus is curved, and consequently there is a grave objection to the use of mercury for calibration purposes. Mercury is unsuitable because its surface tension, and therefore the shape of the meniscus, is liable to be seriously altered by the presence of traces of impurities, and also because, owing to irregularities in the agitation of the mercury in the tube, even when the tube is clean otherwise than by the adhering layer of moisture, the angle of incidence of the mercury surface with the walls of the tube may vary within wide limits, influencing the shape of the meniscus thereby. There is, besides, the possibility that small air pockets will remain between the mercury and the glass at the angular corners at the bottom of sediment tubes.

No data are given in the *International Critical Tables* directly connecting the meniscus correction for water with the diameter of the tubes, but a table is given in Vol. I, p. 73, correlating values of $g\rho\frac{r^2}{\gamma}$ with $\frac{V}{r^3}$ computed from tables, derived from theoretical considerations, by Bashforth and Adams in "Capillary Action," for a liquid with meniscus concave upwards, and angle of incidence of liquid surface with cylinder = 0° , from which a table of meniscus corrections for water can be interpolated, where

- V = volume of meniscus = meniscus correction.
- r = radius of circular tube.
- g = acceleration of gravity.
- ρ = difference between specific gravities of air and water.
- γ = surface tension.

and the angle of incidence = 0° infers the use of thoroughly cleaned glass surfaces.

The following table gives the values of the meniscus correction for water at 20° C. in clean glass tubes of circular cross-section for various diameters interpolated from these data. The values for the smaller tubes given in the table are available for calibration of most of the sediment tubes in use, and the larger values may be of use in calibration of gas apparatus.

For comparison, the other published values quoted above are also shown on the table, along with the values of $1/3\pi r^2$.

MENISCUS CORRECTION.

Water at 20° C. Angle of incidence at Surface=0°.

Diameter of Tube. mm.	Meniscus correction.				
	Bashforth & Adams' Data. ml.	Treadwell & Hall Quantitative Analysis. ml.	Sutton's Volumetric Analysis ml.	Winkler, <i>Z. ang. Ch.</i> ml.	$1/3\pi r^2$. ml.
1.0	0.00013		0.00105	0.00013	0.00013
1.5	0.00048				
2.0	0.00103		0.00215	0.00101	0.00105
2.25	0.00145				
2.50	0.0020				
2.75	0.0026				
3.00	0.0033	0.006	0.00465	0.00318	0.0035
3.25	0.0042				
3.5	0.0052				
3.75	0.0063				
4.0	0.0076	0.010	0.0072	0.0070	0.0084
4.5	0.0106				
5.0	0.0142	0.0155	0.0130	0.0128	0.0164
6.0	0.0234	0.022	0.0195	0.0206	0.0283
7.0	0.0353	0.0305	0.0310	0.0308	0.0449
8.0	0.0498	0.0405	0.0420	0.0432	
9.0	0.0666	0.0530	0.0570	0.0592	
10.0	0.0858	0.0670	0.0720	0.0778	
11.0	0.1073	0.0835	0.0950	0.0988	
12.0	0.1309	0.1020	0.1180	0.122	
13.0	0.1566	0.1225	0.1315	0.146	
14.0	0.1830	0.1445	0.1455	0.172	
15.0	0.2104	0.1680	0.1715	0.201	
16.0	0.2390	0.1935	0.1975	0.227	
17.0	0.2679	0.2205	0.2215	0.254	
18.0	0.298	0.2495	0.2460	0.283	
19.0	0.327	0.2800	0.2600	0.312	
20.0	0.356	0.3120	0.2740	0.339	

The most reliable values are those obtained from Bashforth and Adams' work, and they are closely in accord with the values to be expected from other theoretical considerations. All the published results determined by experiment suffer from the practical difficulties involved in the determinations, and are low for wide tubes, but Göckel's and Schloesser's results are very high for narrow tubes. Winkler's results, however, are closer to the theoretical values over the whole table and are extremely good for the narrowest tubes.

The magnitude of the meniscus correction is always less than $1/3\pi r^2$, but approximates to that value when the tubes are narrow. Bashforth and Adams' data show that the values obtained by using the formula $1/3\pi r^2$ for tubes of 2.0, 1.0 and 0.6 mm. diameter are, respectively, 2.4, 0.5 and 0.2 per cent. too high.

For tubes narrower than 1 mm. diameter it is obvious that the corrections can be calculated by assuming that the meniscus surface is a perfect hemisphere, and by using the formula $1/3\pi r^2$.

The correctness of the values applied in calibration does not affect many gas analyses, where, as a rule, small quantities of gas are measured by difference at parts of the burettes where the same correction applies to both readings, but it is of great importance in the calibration of sediment tubes where the total volume is required, and, unfortunately, it is just at the part of the tables where these measurements are affected that the published data show the greatest divergence.

For example, the amounts of sediment from certain liquids and of insoluble dust in air found in practical determinations are of importance at volumes of 0.010 ml. and 0.0010 ml. If the 0.010 ml. were measured in a tube of 3 mm. diameter and the volume noted by a mark, and, after cleaning and drying the tube, the volume of water required to fill to this mark were determined, the actual volume would be $0.010 + 0.0033 = 0.0133$ ml. Applying the correction given in Treadwell and Hall's book, however, namely, 0.006 ml., the apparent volume would be 0.0073 ml., and with Sutton's correction it would be 0.00875 ml.—errors of 27.0 and 12.5 per cent., respectively. The corresponding error in the calibration of 0.0010 ml. in a tube of 1 mm. diameter, using Sutton's correction, is much greater, the volume plus meniscus being 0.00113 ml., the correction 0.00105 ml., and the difference 0.00008 ml., which is less than one-tenth of the volume actually measured.

Some tubes calibrated for this purpose can be seen by inspection to be incorrect, probably from this cause, at the lowest graduation. The same error occurs, of course, at every graduation and, if the Treadwell and Hall meniscus correction has been used in calibrations of a tube of 3 mm. diameter, the volumes corresponding with marks at 0.010, 0.020, &c., ml. are actually 0.0127, 0.0227, etc., ml.

No attempt has been made in this paper to estimate the degree of accuracy which can be reached in the application of the theoretical values here given to the calibration of vessels. The errors in the values hitherto published, however, are much greater than those arising in practical work.

I have to thank Dr. S. Sugden for his help in confirming the meniscus corrections calculated above, and Sir Robert Robertson for permission to publish this paper.

GOVERNMENT LABORATORY,
STRAND, W.C.2.

The Composition of Irish Winter Butter.

By P. S. ARUP, M.Sc., F.I.C., A.C.G.I.

(Read at the Meeting, October 2, 1929.)

THE fact that genuine Irish winter butter gives abnormal results on analysis has long been known, and was last demonstrated by Brownlee in 1925 (*Proc. Royal Dublin Soc.*, 18, [N.S.], 49). As is well known, calving takes place almost exclusively during one season of the year in Ireland, and abnormally low Reichert-Meissl values are observed at the end of the lactation period. It has been pointed out on several occasions in the Journal of the Department of Agriculture and Technical Instruction, both by Mr. G. Brownlee, B.Sc., F.I.C., and by Mr. A. Poole Wilson, Chief Inspector in Dairying of the Department, that, under these conditions, the assumption of the minimum standard of 24 for the Reichert-Meissl value is likely to lead to unjust prosecutions. As there still appears to be a tendency to apply this standard in too rigid a manner, it was decided by the Department of Agriculture to extend these investigations, and also to examine the validity of the Avé-Lallemant test as a criterion of genuineness for butter with abnormally low Reichert-Meissl values. It is stated in some standard text books that the Avé-Lallemant value may be so used, although Brownlee (*loc. cit.*) has thrown considerable doubt on the validity of this claim.

A total of 310 samples of cream or butter was taken from 30 creameries and 2 agricultural schools in the Irish Free State by Inspectors of the Department of Agriculture in such a way that the genuineness of the samples could be guaranteed. The creameries were sampled during the period from October 27th, 1927, to March 31st, 1928, as nearly as possible at fortnightly intervals.

Most of the samples were taken as cream and, except in the case of those from the agricultural schools, they represent the mixed milk of numbers of herds. The figures obtained are, therefore, likely to show less variation from the normal than would have been the case if single herds had been sampled; they are, however, quite comparable with the figures obtained by Brownlee (*loc. cit.*).

SEPARATION OF FAT.—It was found convenient to separate the fat from the cream samples by first freezing them, whereby the cream emulsion was broken, and then warming them to about 60° C. The fat then collected in a clear layer which could easily be dealt with. In a few cases where the fat globules in the cream were exceptionally small, as may be the case at the end of the lactation period, it was necessary to repeat the freezing and heating in order to obtain a good separation.

TABLE A.
FORTNIGHTLY AVERAGES.

Period.	No. of samples.	Maximum.				Minimum.			
		R.M.	Pol.	K.	Refract. Zeiss ^o at 40° C.	R.M.	Pol.	K.	Refract. Zeiss ^o at 40° C.
27/10/27-15/11/27	37	24.96	1.71	18.17	44.7	26.8	2.40	19.5	46.0
16/11/27-30/11/27	34	24.23	1.74	17.65	44.4	28.2	2.70	21.7	45.2
1/12/27-15/12/27	24	23.80	1.68	17.77	44.2	29.7	2.85	20.9	45.4
16/12/27-31/12/27	22	23.81	1.75	17.78	43.6	28.8	2.45	21.7	45.0
1/1/28-15/1/28	24	24.65	1.88	18.20	43.8	28.9	2.95	20.6	44.7
16/1/28-31/1/28	40	25.77	1.80	19.06	44.2	29.4	2.85	23.0	45.9
1/2/28-15/2/28	32	26.98	1.89	19.81	44.1	31.9	3.20	22.0	45.5
16/2/28-29/2/28	30	28.55	2.10	21.18	44.1	31.6	3.05	24.3	45.3
1/3/28-15/3/28	35	29.52	2.03	21.60	44.1	32.9	2.85	23.6	45.5
16/3/28-31/3/28	32	30.11	2.12	21.71	44.0	32.7	3.00	23.8	45.2

TABLE B.

Creamery.	Date.	R.M.	Pol.	Kirsch.	K. as percent. of R.M.	Refract. Zeiss ^o at 40° C.	Saponification value.	Avé-Lallement value.
A	23/12/27	20.4	1.70	14.6	71.6	45.0	219.4	+11.3
B	23/12/27	20.6	1.85	15.1	73.3	45.0	220.0	+6.5
C	14/12/27	20.8	1.50	16.0	77.0	44.8	220.1	+9.3
C	23/11/27	21.9	1.45	16.5	78.6	43.2	220.9	+14.0
D	14/12/27	21.6	1.35	15.7	72.7	44.5	220.9	+11.9
E	19/12/27	21.2	1.45	16.5	77.8	43.8	219.7	+14.0
F	21/12/27	21.6	1.40	16.3	75.4	43.9	222.9	+14.1
G	7/1/28	21.7	1.60	15.9	73.3	43.9	220.9	+13.6
B	21.6	21.6	1.60	16.4	75.9	44.2	225.0	+0.6
H	16/1/28	21.7	1.70	16.3	75.1	45.0	225.3	+4.3
I	23/11/27	22.6	1.65	15.9	70.0	44.1	227.7	+5.3
J	16/12/27	22.8	1.70	17.3	76.0	43.8	227.7	+8.1
K	22/12/27	22.3	1.50	17.1	76.7	44.6	225.0	-3.5
L	31/12/27	22.9	1.80	17.5	76.4	43.3	225.0	+6.0
M	14/12/27	23.1	1.80	18.0	77.9	44.4	221.0	+11.7
N	23/12/27	23.8	1.90	18.5	77.7	44.0	224.4	+8.4
O	23/12/27	23.8	1.85	18.3	76.9	43.3	224.4	+9.0
P	14/12/27	24.8	1.65	19.2	77.5	44.1	225.5	+8.7
Q	14/12/27	24.9	1.75	19.1	76.6	42.8	225.0	+11.0
R	23/12/27	25.5	1.95	19.0	75.1	44.0	225.5	+7.5
R	2/1/28	25.5	2.00	19.0	74.5	44.2	226.1	+7.7
S	26.7	26.7	2.95	18.9	70.7	42.0	235.0	-11.1
P	28/3/28	31.4	2.55	22.4	71.4	43.7	233.4	-13.3

The fortnightly average results with maxima and minima are shown in Table A. Full particulars of the samples which were also tested by the Avé-Lallemant method are given in Table B.

REICHERT-MEISSEL VALUES.—The following table shows particulars of the number of samples giving Reichert-Meissl values under 24:

R.M.	Number of samples.	Per-centage.	Dates of samples.
Below 20 Nil	Nil	
20-20.9 incl.	.. 3	0.9	14/12/27 to 23/12/27
21-21.9 8	2.6	23/11/27 to 16/1/28
22-22.9 16	5.2	23/11/27 to 21/1/28
23-23.9 23	7.4	31/10/27 to 31/1/28
Total under 24 ..	50	16.1	31/10/27 to 31/1/28

The last sample with Reichert-Meissl value under 25 was taken on February 14th, and the last with a value under 26 on March 6th. The average dropped below 24 during a period including approximately the last 9 days of November and the first three weeks of December. All the samples giving Reichert-Meissl values below 24 occurred from October 31st to January 31st inclusive. During this period 184 samples were taken, the percentage of these showing Reichert-Meissl values below 24 being 27.2.

Brownlee (*loc. cit.*) found, in 1924-25, that all samples with Reichert-Meissl values below 24 occurred from October 26th to February 6th inclusive, and that, of the 75 samples taken during this period, 81 per cent. were below the standard of 24. Of the total number, 5 were below 20, as compared with none in the present (1927-28) series, and 20 were below 21, as against 3 in 1927-28. The twelve creameries sampled in 1924-25 were all included in the present series, and the difference between the two sets of figures points to an improvement in Irish Dairy farming, as a result of the activities of the Department under the Dairy Produce Act of 1924. The factors responsible for the change are: (1) A tendency to extend the calving period, and (2) a certain improvement in the treatment of the cows during the winter.

The samples from the Department's Agricultural Schools at Ballyhaise and Clonakilty in the present series, 20 in all, deserve special mention, for in no case did they give Reichert-Meissl figures below 26. This is explained by the fact that calving in these places is not confined to one season of the year, as is generally the case in Ireland, and also by superior conditions of feeding and shelter. Similar effects are noted with regard to the Polenske values below.

POLENSKE VALUE.—The maximum value recorded was 3.20 in connection with a Reichert-Meissl value of 31.4, and the minimum 1.15 in connection with a Reichert-Meissl value of 22.2.

The following Table shows average, maximum, and minimum Polenske values obtained with progressive Reichert-Meissl values:—

Number of samples.	R.M. (-0.5 +0.4.)	Polenske.			Variation between max. & min.
		Average.	Max.	Min.	
15	22	1.50	1.70	1.15	0.55
22	23	1.60	1.80	1.35	0.45
43	24	1.65	2.00	1.40	0.60
56	25	1.70	2.25	1.35	0.90
35	26	1.90	2.40	1.45	0.95
26	27	1.95	2.85	1.55	1.30
22	28	2.05	3.05	1.60	1.45
15	29	2.20	2.85	1.75	1.10
26	30	2.10	2.85	1.65	1.20
30	31	2.25	3.20	1.60	1.60

For Reichert-Meissl values of 22-26, inclusive, the average Polenske values agree very closely with those given by Bolton in his "Oils, Fats and Fatty Foods." For increasing Reichert-Meissl values above 26, the averages begin to fall below Bolton's figures, being 0.95 less at Reichert-Meissl 31.

All the creameries sampled, except the Agricultural Schools at Ballyhaise and Clonakilty, tended to produce butters showing Polenske values below the normal; this is reflected by the somewhat large differences between maximum and minimum values in the above table for Reichert-Meissl values of 26 and over; all the maximum Polenske values recorded, however, fall within 0.5 of the standards given by Bolton, thus confirming his criterion indicating freedom from adulteration with coconut or palm-kernel oils. In contra-distinction to the rest of the creameries sampled, 10 samples from Ballyhaise averaged:—Reichert-Meissl value, 28.3; Polenske value, 2.5. Ten samples from Clonakilty averaged Reichert-Meissl value, 29.0; Polenske value, 2.75; that is, they gave normal Polenske values, for reasons similar to those discussed in connection with Reichert-Meissl values above.

KIRSCHNER VALUE.—This was determined by the standard method, with the use of aluminium wire in the distillation. The minimum value recorded was 14.6 in connection with a Reichert-Meissl value of 20.4, and the maximum was 24.1 in connection with a Reichert-Meissl value of 32.7. The average Kirschner value of all the samples was 73.4 per cent. of the average Reichert-Meissl value. On individual samples, this percentage varied from 68.0 to 79.6, but showed no co-ordination with variations in the Reichert-Meissl value or other factors.

The relationship between Kirschner and Polenske values is shown in the following table:

No. of samples.	Kirschner value (-0.5 +0.4.)	Polenske value.			Variation between max. & min.
		Average.	Max.	Min.	
30	17	1.55	1.85	1.15	0.70
69	18	1.70	2.40	1.35	1.05
67	19	1.85	2.95	1.45	1.50
27	20	1.95	3.05	1.60	1.45
22	21	2.15	2.80	1.55	1.25
39	22	2.15	2.85	1.60	1.25
25	23	2.20	3.00	1.65	1.35

The agreement with the figures published by Bolton and Revis and Richmond is not so close here as in the case of the relations between the Reichert-Meissl and Polenske values, and in several cases the maximum Polenske values are too high to fit in with the criterion for determining the presence of coconut oil or palm-kernel oil.

AVÉ-LALLEMANT VALUE.—Twenty-two samples with Reichert-Meissl values varying from 20·4 to 25·5 showed Avé-Lallemand values varying from +14·1 to -3·5, only one sample giving a negative value. Two samples having Reichert-Meissl values of 26·7 and 31·4 showed Avé-Lallemand values of -11·1 and -13·3, respectively (see Table B). Brownlee (*loc. cit.*) found values varying from -25·0 to +10·4, 20 samples out of a total of 112 giving positive results.

The conclusion of Brownlee that the Avé-Lallemand value cannot be taken as a criterion for distinguishing between genuine butters having low Reichert-Meissl values on the one hand, and adulterated butters of higher Reichert-Meissl values on the other, is confirmed here. It would appear that butters with low Reichert-Meissl values had not been sufficiently investigated in this connection before the matter was taken up by Brownlee, and that the Avé-Lallemand value, in common with most of the other commonly determined figures, merely tends to serve as a confirmation of the Reichert-Meissl value.

SAPONIFICATION VALUE.—In 24 samples this varied from 219·4 to 235·0, thus confirming the usually accepted limits for pure butter.

THE COMPOSITION OF IRISH WINTER BUTTER, 1928-9.

A series of analyses similar to that reported for the winter season of 1927-8, was carried out for the season of 1928-9. The results confirm those previously obtained, so that a brief summary will suffice. Out of a total of 270 samples, representing 36 creameries and 3 agricultural schools, taken from November 1st, 1928, to February 23rd, 1929, those showing R.M. values below 24 were as follows:

REICHERT-MEISSL VALUE.

R.M.	No. of Samples.	Percentage.	Dates of Samples.
Below 20	Nil	Nil	
20-20·9	3	1·1	5/12/28 to 17/12/28
21-21·9	17	6·3	19/11/28 to 3/ 1/29
22·0-22·9	34	12·6	1/11/28 to 18/ 1/29
23·0-23·9	34	12·6	1/11/28 to 25/ 1/29
Total	88	32·6	1/11/28 to 25/ 1/29

The average figures for fortnightly periods were as follows:

Period.	No. of samples.	Average.	
		R.M.	Pol.
November 1st-15th	28	24.2	1.69
„ 16th-30th	37	23.3	1.61
December 1st-15th	32	22.9	1.63
„ 16th-31st	31	23.5	1.78
January 1st-15th	34	25.5	1.85
„ 16th-31st	36	26.5	1.79
February 1st-13th	28	27.0	1.75
„ 14th-23rd	30	28.3	2.00

The unusually cold weather which prevailed all over the country from the 11th to the 17th of February had no noticeable effect in checking the upward tendency of the Reichert-Meissl values, and it may be concluded that the predominating factor influencing these values is the lactation period.

POLENSKE VALUE.—The minimum recorded was 1.30 in connection with R.M. values of 21.1 and 24.9. The maximum was 3.40 with R.M. of 29.2. All the Polenske values taken in connection with their corresponding R.M. values fell within the limits generally laid down in the literature for genuine butter. When the R.M. values increase during the early part of the year, the Polenske values do not increase at the same proportionate rate, and are thus somewhat below the average. In the case of the samples from the three agricultural schools, however, the Polenske values were higher, and, generally speaking, about the normal. In these particulars the experience of last year is confirmed.

KIRSCHNER VALUE.—This was determined on 136 samples, mostly those having R.M. values below 24, and was found to vary from 67.3 to 81.2 when expressed as a percentage of the corresponding R.M. value. It was not found possible to trace any connection between these variations and any other factor.

BRINE-SOLUBLE AND BRINE-INSOLUBLE VALUES.—These were determined by Elsdon and Smith's modification of Gilmour's method (ANALYST, 1927, 52, 317). The distillation process is the same as in the Reichert-Meissl-Polenske process except that 100 c.c. are distilled instead of 110 c.c., so that the total volatile acids were consistently lower than in the Reichert-Meissl process. In order to ascertain whether the salting-out process gives more consistent results than the usual method, the following comparisons were made:—Seventy samples showed ordinary Polenske values varying from 5.5 to 10.4 per cent. of the total volatile acids, and brine insoluble values from 10.1 to 23.8 per cent. The seven highest and seven lowest Polenske percentages varied from 5.5 to 5.8, and from 8.3 to 10.4 respectively, whilst the corresponding percentage figures for the brine-insoluble were 10.1 to 12.0 and 17.7 to 23.8, respectively.

The following table shows some typical results obtained with butter of low Reichert-Meissl values; the brine-insoluble values are about twice the Polenske values, as Elsdon and Smith found to be the case with butters of higher Reichert-Meissl values. The brine soluble values are slightly higher than the corresponding

Kirschner values. As a measure of the volatile acids in pure butter, the brine method does not appear to offer any particular advantages over the Reichert-Meissl-Polenske method, but there is a possibility that it might do so in the case of mixtures containing palm nut or coconut oils. The method was of course primarily designed for the estimation of butter in margarine, and for this purpose it offers some advantages over the Kirschner method, being simpler and less liable to experimental error.

Date of sample.	R.M.	Polenske.	Kirschner.	Kirschner as per cent. of R.M.	Brine.		Refractive. index, Zeiss ^o at 40° C.
					Sol.	Insol.	
5/12/28	20.8	1.50	16.2	77.9	17.6	3.20	46.9
17/12/28	20.7	1.70	14.5	70.0	17.6	2.35	46.6
"	20.8	1.50	14.5	69.7	17.3	2.55	46.9
19/11/28	21.8	1.35	16.1	74.0	19.0	2.55	45.2
26/11/28	21.5	1.45	16.0	74.3	17.9	2.55	47.0
1/12/28	21.3	1.40	16.4	76.9	18.4	2.20	46.9
3/12/28	21.8	1.50	15.6	71.5	18.2	2.80	46.9
"	21.1	1.55	17.1	81.2	18.6	3.20	46.9
"	21.7	1.65	16.8	77.3	18.8	2.45	46.9
5/12/28	21.5	1.35	17.2	80.2	17.5	2.85	46.4
7/12/28	21.9	1.65	16.5	73.8	18.0	2.45	45.5
10/12/28	21.5	1.55	16.2	75.3	17.8	2.60	46.9
12/12/28	21.1	1.50	16.4	77.7	17.1	2.25	46.8
"	21.5	1.60	16.0	74.6	17.8	2.40	46.7
18/12/28	21.7	1.60	15.9	73.3	18.8	2.75	45.8
19/12/28	21.3	1.50	15.4	72.3	18.7	2.10	46.4
22/12/28	21.1	1.30	15.1	71.5	18.5	2.40	45.9
24/12/28	21.7	1.60	15.2	70.0	18.5	3.05	45.8
31/12/28	21.9	1.70	16.3	74.6	18.7	2.40	45.5
3/ 1/29	21.6	1.65	15.5	71.6	18.4	3.00	—
1/11/28	22.8	1.50	17.6	77.2	19.0	3.05	44.8
"	22.6	1.60	16.8	74.5	17.4	3.20	45.4
19/11/28	22.3	1.45	17.2	77.3	19.3	2.40	46.3
"	22.7	1.40	16.7	73.7	19.4	2.70	47.0
"	22.6	1.45	16.1	71.3	19.0	2.75	45.5
"	22.1	1.45	16.1	75.3	19.0	2.50	45.7
"	22.8	1.65	17.7	77.9	19.4	2.95	45.7

I wish to express my thanks to the Department of Agriculture, Irish Free State, for permission to publish the above matter.

DEPARTMENT OF AGRICULTURE,
BUTTER TESTING STATION, DUBLIN.

DISCUSSION.

The PRESIDENT said that it was very disturbing that we should have winter butters giving such abnormal values. It raised difficulties in the interpretation of analytical results. He was much obliged to Mr. Arup for coming from Ireland to read this paper. He referred to many members who regretted their inability to be present, and read some observations sent by Mr. G. D. Elsdon. They were

fortunate in having with them Mr. F. Dickinson, of the Chemical Research Division, Ministry of Agriculture, Northern Ireland, who had been so good as to come from Ireland for this meeting.

Mr. F. DICKINSON (Department of Agriculture, Northern Ireland), speaking also on behalf of Dr. G. S. Robertson, said that it was interesting that both Northern Ireland and the Free State should have been conducting independently, and without previous knowledge of each other's activities, an investigation as to the behaviour of butter towards the Reichert-Meissl test. Both investigations appeared to have begun about the same time; that in Northern Ireland started in June, 1927, and was still in progress, whilst Mr. Arup's started in November, 1927. They had also been examining at regular intervals butter from seven creameries, three of the Ministry's farm schools, where a uniform milk yield was maintained, throughout the year, and the influence of lactation was, therefore, minimised; and also farm butter produced from the herds of seven private breeders, included in which were Jersey, Kerry and Crossbred Shorthorn herds.

In the main, their results were in keeping with those obtained by Mr. Arup. The results of the two years' investigation showed that there was a big drop in the Reichert-Meissl value in August, and that during 1927-28 that value was below 24 during September, October, November, and December. During January there was a marked recovery, and from then onwards the figure remained normal. The corresponding curves for the three schools and the private herds were similar; and as a more or less even flow of milk was maintained at these three Institutions, it was difficult to agree with Mr. Arup that the lactation period was mainly responsible for the low Reichert-Meissl values during September to January. It was because it was clear to them that some factor other than the period of lactation was involved, that they decided to carry on the investigation over a period of years before publishing the figures.

In this connection the results for 1928-29 were interesting. The Reichert-Meissl figures were very much higher. Mr. Arup accounted for the marked improvement in Free State butter by crediting it to the beneficial activities of the Free State Dairy Produce Act. Northern Ireland had not yet a Dairy Produce Act; nevertheless, there was manifested the same tendency towards an extension of the calving period and better feeding in the winter. Such changes, however, were only gradual, and it was inconceivable that they could account for the very marked improvement in the Reichert-Meissl values for the season 1928-1929, when compared with 1927-1928.

Some other factor was clearly operating, possibly a climatic factor which influenced the nutritional value of the grass and hay. There was a suggestion from their results that a shortage of minerals might be associated with the production of butter-fat with a low Reichert-Meissl value.

One other point might be of interest to members. They were considering, pending the conclusion of the investigation, the issue of a monthly Reichert-Meissl value, which would be circulated to the Public Analysts in Northern Ireland, the number being based on the determinations on butter made at Northern Ireland creameries under the supervision of the Ministry's staff.

Mr. E. R. BOLTON, in expressing his appreciation of the utility of the figures the author had given, observed that he could not help regarding them with mixed feelings. Although some criticism might be made of the method of separating the fat, he himself was clearly of opinion that the method, though unfortunate, did not affect the accuracy of the figures, which he accepted without question.

From the scientific point of view, it was interesting once more to have confirmation of the fact that, when cattle were subjected to certain conditions, they

actually produced a butter-fat that was not of the normal composition of the butter everyone was accustomed to receive when they asked for a pound of butter over the counter. This, he thought, was indeed very unfortunate, as he feared the publication of this paper would have the effect of causing quite unjustified damage to the Irish butter trade. Everyone knew that Irish butter was an extremely good product; but if the public were now to be told that during certain times of the year it became an abnormal product, and would, by the tests already accepted, be held to be adulterated, it would be very difficult to persuade them that this abnormality might not also mean inferiority.

At this point he would like to defend certain tests upon which he had always placed reliance, and, in particular, the Avé-Lallemant test. This test, in his opinion, was a rapid and reliable method of finding out whether a butter was, or was not, of normal composition and unadulterated. It was not vitiated by the presence of mixtures of coconut with other fats, which vitiated certain other tests. In the case of these Irish butters the Avé-Lallemant test showed that the butters were not of normal composition; he regarded this as confirming, rather than shaking, his confidence in the test.

The analyst, therefore, was faced with a very difficult position, and if the analyst were to become an advocate—which he should never be—he would find a great deal to say. On the one hand, he might claim that if a cow were not treated in a normal manner the butter-fat which resulted could not be regarded as the product that the public expected when they demanded butter. If, on the other hand, he wished to justify this butter, he might say that the product had come from the animal, nothing had been added to it, and it should be regarded as genuine butter.

It, therefore, became more an ethical question than an analytical one, and he asked Mr. Arup if he could give the meeting some guidance on the light in which, in his opinion, this question should be regarded. Mr. Arup had said of the cattle, "as a rule they are very badly fed indeed," and what he (Mr. Bolton) asked was whether good feeding, better environment, and a spreading-out of the calving period would not have the effect of rendering this butter normal; and, in view of the fact that the Irish Dairy Produce Act, 1924, had (as Mr. Arup had said) brought about a great improvement, he enquired whether it was, or was not, a fact that the public might expect the farmers to put this butter question right themselves (and relieve the analyst of the whole question of deciding what should be done with an admittedly abnormal butter) by the simple process of removing such abnormal butters from the market by improving their methods of farming.

Mr. W. WRIGHT (Inspector of New Zealand Dairy Products, London, of the Dairy Division, New Zealand Department of Agriculture) said that he felt that, although he was the guest of the Society that evening, he was rather an outsider, since he was more conversant with the technology of dairying than with analytical chemistry. He had been very interested in the subject which had been under review that evening. With regard to the irregularity of the butter-fat during the period mentioned, he pointed out that there were several factors which, in his opinion, would affect the butter-fat in milk. For instance, general health and care of the dairy stock, climatic conditions, such as abnormal rainfalls, lack of sunshine and cold windy weather, the quality of the pastures, and also method of feeding and treatment of the stock during the lactation period. As the lactation period of cows progressed there did appear to be a change which took place when the lactation period was drawing to a close, and for that reason the milk and butter were at such times less attractive or palatable for human consumption. He felt that before steps were taken to prosecute in the matter of faults in the constituents of milk, butter or cheese, there should be a reasonable margin of error

allowed in chemical analysis. Owing to the fact that there was such a variable percentage of butter-fat and solids-not-fat in milk, and since changes in the butter-fats might be brought about by abnormal conditions, products that were absolutely free from adulteration might be of such quality that, when analysed, they might be classified as having been adulterated. There was no doubt that Mr. Arup's paper had opened up a very wide question, and, if he might make the suggestion, he thought that, when possible, in future observations regarding the fat percentage of butter, a record should be kept of the condition of the animals from which the milk was obtained, and of the pastures, feeding and climatic conditions during the research period. In his opinion, it was probable that valuable data would thus be obtained which would do much towards solving the problem under discussion.

Mr. A. MORE said that the problem for the analyst was to say whether a butter was genuine or not, and for this purpose the Reichert-Meissl value was the most important factor. The work of the Departmental Committee in 1901-2 had shown that genuine butter from Ireland, and also from England and Scotland, had low Reichert-Meissl values at the same time of year as those shown in the present paper, and that Committee had suggested the adoption of a value of 24 as a presumptive standard only. The chemist was apt to be misled in judging the quality of butter by the Reichert-Meissl value, but there was no evidence to support the assumption that butter of low Reichert-Meissl value was necessarily inferior in quality. This paper would have the effect of preventing prosecutions based solely on a presumptive standard. He did not think that a positive Avé-Lallemant value was a criterion of adulteration. He produced a chart of Avé-Lallemant's original results (*Z. Nahr. Genussm.*, 1907, p. 321), in which all the values were negative, but the lowest Reichert-Meissl value was 24.6, and the curve passed over, if continued, to positive values, at a Reichert-Meissl value of 25. Positive results which he had obtained on butters with Reichert-Meissl values of 21 agreed with those of Mr. Arup.

Mr. K. A. WILLIAMS remarked that the general tendency of the analytical figures for poor butters was exactly the same as for adulterated butters. In particular, he had found that the relation between the Reichert-Meissl and Avé-Lallemant values, shown by Mr. More for butter-fats of varying quality, was identical with that for adulterated butter-fats. It followed that, at the present time the assumption of arbitrary limits was the only possible means available for deciding whether a sample was pure; he, personally, would welcome the discovery of a factor which would determine purity without reference to such limits.

Dr. H. E. COX said that the introduction of the factor " $b-(200+c)$ " in the Avé-Lallemant process was artificial and misleading; the change of sign from $-$ to $+$ gave a false sense of security which was not warranted by the change of a few units in the barium oxide values. One could not be sure of saponification values nearer than about 1 unit in terms of potassium hydroxide, and a larger figure in terms of barium oxide. He disagreed with the view that the butter was inferior; the only point to his mind, as a Public Analyst, was whether the purchaser was prejudiced, and it could not be said that he was, simply because he got a little less butyric acid and a little more of the higher fatty acids, as at present we knew nothing of their relative dietetic values. He urged the need for a quick method for the determination of the melting point of the sterol acetates, workable on the small amount of fat usually available to the Public Analyst, after he had made his other tests.

Mr. MORE here offered to let Dr. Cox know the details of a method which he had found to give satisfactory results with 15 grms. of fat, and which had been

given to him by Dr. van Sillevoldt of the Butter Control Station at Leiden, Holland.

The PRESIDENT remarked that there was no very certain relation between Reichert value and commercial quality, but it seemed that these abnormally low Reichert values were associated with bad farming practice, semi-starvation of the cattle, and so forth. He supposed that the more a natural product like butter was investigated, the greater was the probability of the disclosure of occasional abnormality. It really came to this, that by abnormal, and generally undesirable, conditions, abnormal butters could be produced. If it could be shown, and the paper and the discussion did so show, that by proper farming normal, and not abnormal, butter was obtained, then it seemed to be desirable in the public interest that a minimum Reichert value should be established by law. He hoped that the Ministries of Agriculture of the Free State and of Northern Ireland, and of England and Scotland too, would use their influence to ensure that farming should be such that the produce was what was given by good farming. Extreme insistence on the principle that anything that came from the cow was "genuine" was damaging the public.

Mr. G. D. ELSDON (in a written communication) said that the Avé-Lallemant process had, unfortunately, not fulfilled the hope that it at first aroused, and Mr. Arup's work still further discouraged its use. The process was somewhat lengthy, and the figures obtained were sensitive to quite small experimental errors, and afforded very little assistance in coming to a final decision as to the genuineness of any particular sample. It was, of course, now firmly established that butter obtained from milk taken towards the end of the lactation period was quite likely to be deficient in volatile acids, but this fact should be taken as an exhortation to farmers to arrange their calving so that butters with low Reichert values should not be produced. It was never safe, of course, to report a butter as adulterated on the evidence of the Reichert value alone, unless this was considerably under 20. It was possible that some information might be obtained from the differences between the brine-insoluble figure and the Polenske figure, as this would be a measure of the volatile acids of high molecular weight. He had not, as yet, had an opportunity of examining this suggestion. It might also be valuable if Mr. Arup carried out some work on Irish butters on the lines followed by Atkinson (ANALYST, 1928, 53, 520).

Mr. ARUP, replying, said that with regard to the question whether low Reichert-Meissl values indicated poor quality in butter, samples had been examined by experts, with a view to determining this question, and it had been found that there was no connection at all between these factors. There was, therefore, no question of prejudice to the public, but the matter was one which might give some trouble to the analyst. He agreed with Dr. Cox that the Avé-Lallemant formula, giving, as it did, positive and negative values, invited judgments which might be too rigid. He would wish to see the whole problem attacked from a different point of view, as it appeared that the possibilities of volatile acid determination had been exhausted. Other butter-producing countries had experienced the same trouble, notably Holland, and it had been generally agreed that it arose in connection with the lactation period.

If it were a question of the addition of margarine to butter, the sterol acetate method was very useful, as vegetable oils or fats were sure to be contained in any margarine; and the use of hardened vegetable oils, now very common, did not, in his experience, vitiate the results of this test; hardened oils had largely come to replace animal fats. With the use of digitonin, the method was very convenient, and was capable of detecting as little as 2.5 per cent. of margarine.

He had been very interested in Mr. Dickinson's remarks; it was a remarkable coincidence that the two Ministries had been doing identical work, and he hoped that in future it would be possible for them to co-operate. He had not examined a large number of samples systematically before October of each year. In Ireland, cows were very much more dependent upon the grass than in many other countries, as very little roots and meal cakes were used, and so were dependent upon climatic conditions. The feeding at the agricultural schools during winter consisted of hay, with roots and palm-kernel cake. The average farmer only gave palm-kernel cake in a very few cases.

Reference to the paper would show that no attempt had been made to draw conclusions from a comparison of the results of 1927-8 with those of 1928-9, but the results quoted there were compared as a whole with those obtained by Mr. Brownlee for 1924-5. It was recognised that there would be very little use in comparing results of consecutive years, for reasons very similar to those mentioned by Mr. Dickinson.

A Study of the Methods of Determining Boron Compounds in Food and Drugs.

By A. SCOTT DODD, B.Sc., Ph.D., F.I.C.

(*Work done under the Analytical Investigation Scheme.*)

PART I. HISTORICAL REVIEW.

IN the early days of the Food and Drugs Acts, the officials charged with the detection of adulteration were chiefly concerned with the presence of boron compounds in quantities sufficient to be deemed injurious to health, and with their determination with sufficient accuracy to avoid challenge. In those days the methods were somewhat elaborate and crude, and, in the absence of the discovery of suitable conditions under which indicators could be employed, depended upon the formation of weighable compounds of boron.

THE DISTILLATION METHOD.—The separation of the boric acid from the organic constituents of food was then found to be most reliably effected by distillation in presence of methyl alcohol and an acid. This method is usually associated with the name of Gooch, but it appears to have originated somewhat earlier than Gooch's publication (*Proc. Amer. Acad. Arts and Sciences*, 1886, **22**, 167), as it is referred to by T. Rosenbladt (*Z. anal. Chem.*, **26**, 18). It is, however, quite possible that these investigators may have made the discovery independently.

For many years the distillation method was, and still is, recognised as affording accurate results, and chemists, though satisfied that all the boric acid had distilled, were anxious to ascertain the most reliable method of finally determining it in the distillate. As already mentioned, no trustworthy titration method had been devised, so the boric acid was at first determined gravimetrically.

FIXATION OF BORIC ACID.—T. Rosenblatt (*loc. cit.*) fixed it in the distillate by the addition of a weighed quantity of magnesia, evaporating and igniting. Gooch, recognising that magnesia did not fix the boric acid completely, recommended the use of caustic lime. Penfield and Sperry (*Amer. J. Sci.*, **30**, [iv], 222), in view of the difficulty of igniting to constant weight a comparatively large quantity of caustic lime, modified the process. Cassal (*ANALYST*, 1890, **15**, 375) suggested further improvements, but both modifications failed to remove the difficulty of igniting a gramme or more of lime to a constant weight in a platinum basin. Blount (*ANALYST*, 1891, **16**, 144) stated that the difficulty was overcome by using a muffle furnace.

The use of lime for fixing boric acid is due to H. Gilbert (*Report Anal. Chem.*, Vol. V, p. 375), so that the method attributed to Gooch is really a combination of Rosenblatt's distillation method and Gilbert's ignition process.

Otto Hehner (*ANALYST*, 1891, **16**, 141) investigated the use of other chemical compounds as substitutes for lime. He tried ammonia, but the results of his experiment merely confirmed the observation of Bodewig (*Z. anal. Chem.*, 1884, **23**, 149), that boric acid is volatile in presence of ammonia. By substituting sodium carbonate for ammonia, Hehner found it almost impossible to obtain constant weights. According to Bloxam, one molecule of boric acid displaces, on gentle ignition, one molecule of carbonic acid, but on strong heating (to red heat) it displaces from 1.5 to 2.3 molecules; while, according to Schaffgotsch, one equivalent of H_3BO_3 expels all carbonic acid from two molecules of sodium carbonate. Hehner's figures are more comparable with those of Bloxam, but show that sodium carbonate does not give reliable results.

Hehner found that one molecule of sodium phosphate (Na_2HPO_4) is capable of binding two molecules of H_3BO_3 , the resulting mass consisting of sodium metaphosphate and borax. He found that very good results may be obtained by the use of sodium phosphate, which has many advantages compared with lime.

EARLY VOLUMETRIC METHODS.—Investigators next turned their attention to the quest for a reliable volumetric method of estimating boric acid. Various indicators were suggested, but none gave satisfactory results. Permentier (*Compt. rend.*, **113**, 41) made two titrations, using two indicators—helianthin and litmus—and reckoned as boric acid the difference between the two titrations.

In 1878 Klein (*Bull. Soc. Chim.*, **29**, 195) first pointed out that additions of certain polyatomic alcohols and sugars had the effect of rendering boric acid solutions more acid. The explanation of such reactions was that combination takes place, with the production of stronger acids. Since then numerous researches have been made, which have added considerably to our knowledge of the subject, and it is now known that not only polyatomic alcohols and sugars form such combinations, but also that a large class of hydroxy compounds reacts similarly.

USE OF SUGARS AND POLYHYDRIC ALCOHOLS.—It was not until 1893 that the action of boric acid on sugars and polyhydric alcohols was made use of in the estimation of boric acid, when R. T. Thomson (*J. Soc. Chem. Ind.*, 1893, **12**, 432)

published his investigations. He found that, when glycerol was added to a solution of a borate, the acidity was increased until, when about 30 per cent. of glycerol, calculated upon the total amount of fluid, was present, the maximum acidity was reached and the total amount of boric acid was sharply indicated, phenolphthalein being the indicator. The end-point of the titration coincided with the entire conversion of the boric acid into sodium metaborate (NaBO_2). Thomson then intimated that he was experimenting on the applicability of his process to the determination of boric acid in food materials. The results of these investigations were published in 1895, and showed a method by which the organic and other interfering substances could be eliminated by ignition in presence of caustic soda and subsequent treatment with solutions of calcium salts. (*Glasgow City Anal. Repts.*, 1895, p. 3.)

K. Thaddéeff (*Z. anal. Chem.*, 1897, **36**, 568) devised a method of determining boron compounds which was really a modification of that of Gooch. It consisted essentially of distillation as methyl borate and fixation and weighing as potassium borofluoride. This method was, however, criticised as defective in two important points by F. A. Gooch and L. C. Jones (*Z. anorg. Chem.*, 1898, **19**, 417), who stated that accuracy can only be attained when the errors due to these defects neutralise one another. They suggested using lime with the addition of sodium tungstate as an absorbent, to prevent loss through the precipitate being hygroscopic.

The reliability of glycerol as an aid to titration, using a method attributed to Jörgensen, was tested by Beythien and Hempel (*Z. Unters. Nahr. Genussm.*, 1899, **2**, 842) and by H. Luhrig (*Pharm. Centralh.*, 1901, **42**, 50). The authors found that less accurate results were obtained by combining Gladding's method with that of Jörgensen than by using the latter alone.

OTHER METHODS.—Various more or less ingenious methods have been suggested, such as the colorimetric methods of C. E. Cassal and H. Gerrans (*British Food J.*, 1902, **4**, 210), of A. Hebebrand (*Z. Unters. Nahr. Genussm.*, 1902, **5**, 1044), and of Bertrand and Agulhon. There is also a gravimetric method with a special distilling tube, utilising the solubility of boric acid in ether saturated with water, which was devised by A. Partheil and J. A. Rose (*Z. Unters. Nahr. Genussm.*, 1902, **5**, 1049).

BORIC ACID IN CREAM, BUTTER AND MARGARINE.—As a result of the report of the Departmental Committee, dated 1901, permitting the use of a limited quantity of boric acid and borax in cream, butter and margarine, steps were taken by some investigators to devise a rapid and accurate method of estimating boric acid in these foods. The ignition of such highly fatty materials presented certain difficulties, and was open to criticism on the grounds that some of the boron compounds were volatilised thereby, even if an excess of alkali was present. T. Macara (*ANALYST*, 1913, **38**, 142) and C. R. Bagshaw (*ANALYST*, 1918, **43**, 138). Richmond and Harrison (*ANALYST*, 1902, **27**, 179) eliminated the difficulty of igniting by merely separating with chloroform and water and taking an aliquot part of the aqueous extract for the estimation. This method, though said to be

accurate, occupied a considerable amount of time; so the authors devised a still more rapid process, which has since been used extensively by dairy chemists. In this method, the boric acid, after treatment, can be titrated without the fat being first removed. Another rapid process, based on coagulation of the milk or cream with copper sulphate and determination of the boric acid in the aqueous portion, is recommended by Richardson and Walton (*ANALYST*, 1913, 38, 140). Many other methods have been devised, with the same end in view, but no one hitherto seems to have made any attempt to investigate fully the effect of igniting boron compounds in presence of varying proportions of fats and oils.

MODIFICATIONS OF TITRATION METHODS.—Various modifications of the methods of titrating boric acid have been suggested. E. B. R. Prideaux (*Z. anorg. Chem.*, 1913, 83, 362) stated that boric acid might possibly be titrated with tolerable exactness by the selection of a suitable indicator, and recommended tropaeoline O. B. H. St. John (*Amer. J. Pharm.*, 89, 8–10) stated that methyl red was a better indicator than methyl orange in the neutralisation of borate solutions previous to the titration of the boric acid in the presence of glycerol and phenolphthalein. J. Prescher (*Z. Unters. Nahr. Genussm.*, 1918, 36, 283) investigated the use of various indicators, and found that, for the final titration, after using either glycerol or mannitol, the most suitable indicator is phenolphthalein. For the neutralisation of borate solutions other indicators have been recommended, such as paranitrophenol, W. Hertz (*Z. anorg. Chem.*, 33, 353) and Sofnol Indicator No. 1, by myself (*ANALYST*, 1927, 52, 459).

SUBSTITUTES FOR GLYCEROL.—Much research has also been carried out, with a view to ascertaining what substances can be substituted for glycerol. Some doubt seems to exist whether a definite compound is formed when glycerol is mixed with a solution of boric acid. The acid complex, formed by the addition of glycerol to boric acid solutions, has been named glyceryl-boric acid and given the formula $(C_3H_5O_2OH)B(OH)$, but some investigators maintain that no compound is formed (R. Dubrisay, *Compt. rend.*, 1921, 172, 1658). The rise in the electrical conductivity observed in solutions of boric acid and poly-hydroxy compounds gives an indication of the stability of the compound formed. Now, glycerol, when added to a solution of boric acid, does not exhibit a very marked positive effect on the conductivity of the solution. This bears out the contention of Dubrisay, and shows clearly that, if a compound is actually formed by the glycerol and boric acid, it is very unstable in aqueous solution.

Thomson (*loc. cit.*) tried to replace glycerol by dextrose and cane sugar, but without success. Vedam (*J. Pharm. Chim.*, 1898, 6, 8, 109) used mannitol, and found that with its use a sharper end-point is obtained than when glycerol is employed.

The stability of the compound formed by boric acid and mannitol is emphasised by the marked increase in electrical conductivity imparted to boric acid solutions by the addition of mannitol, and also by the fact that for the same quantity of boric acid very much less mannitol than glycerol is required for the purpose of titration.

Ageno and Valla (*Gazz. Chim. Ital.*, 1913, **43**, 11, 163), from solubility measurements, concluded that mannitol unites with boric acid in equimolecular proportions. Salts of complex bodies, formed by the union of boric acid with mannitol, sorbitol, and dulcitol, have actually been prepared by Grün and Nossoivitch (*Monatsh.*, 1916, **37**, 409), and, by using the same method, Gilmour (*ANALYST*, 1921, **46**, 3) has prepared the sodium derivative of a complex formed from laevulose and boric acid.

G. Van B. Gilmour (*loc. cit.*) was able to titrate boric acid successfully in the presence of laevulose, dextrose and cane sugar, but found that it was impossible to carry out the titration with lactose. Weak combinations require a large excess of the hydroxy compound; otherwise the complex is hydrolysed before the proper end-point is reached. Laevulose gives excellent results, but the high price of the pure sugar renders its use prohibitive for technical purposes. Invert sugar, on the other hand, is cheaply prepared, and is an excellent substitute. Gilmour's claim to be the first to advocate the use of invert sugar was disputed by J. A. M. Van Liempt (*ANALYST*, 1926, **51**, 293), who pointed out that the use of invert sugar for this purpose had already been suggested by M. Boeseken (*Proc. Roy. Acad. Amsterdam*, 1917, **26**, 3), and worked out by himself (*Rec. Trav. Chim.*, 1920, **39**, 350). It is, however, evident that, although the use of invert sugar had previously been suggested, Gilmour had made the discovery independently, was the first to work it out fully in practice, and was, therefore, justified in claiming to be the first to show the effectiveness and cheapness of invert sugar as a reagent in the titration of boric acid.

Various attempts have been made to estimate boron compounds electrometrically. Mellon and Morris (*Proc. Indiana Acad. Sci.*, 1924, **35**, 85), found that boric acid could not be satisfactorily determined by this means in presence of polyphenols and organic acids. Van Liempt (*Rec. Trav. Chim.*, 1920, **39**, 358), however, found that electrometric determination of boric acid was possible under certain conditions.

To facilitate the titration of boric acid, certain other modifications have been suggested. Alcoholic sodium ethoxide is recommended for the titration of boric acid solutions in the presence of glycerol; the interfering action of carbon dioxide thus being eliminated. Barium hydroxide was also used by some investigators (J. Boeseken and H. Couvert, *Rec. Trav. Chim.*, 1921, **40**, 354). The interference of phosphoric acid can be prevented by the addition of sodium citrate (Kolthoff, *Chem. Weekblad*, 1922, **19**, 449). After neutralisation, addition of mannitol allows of the titration of the boric acid by further addition of sodium hydroxide. Neither calcium nor magnesium salts interfere. W. W. Deerns (*Chem. Weekblad*, 1922, **19**, 480) determined boric acid in presence of phosphoric acid by means of potassium iodide-iodate. The citrate method is not new, having been proposed by Littman (*Chem. Ztg.*, 1898, **22**, 691) and by Pfyl (*Arb. Kais. Gesund. Amt.*, 1914, **47**, 1).

BORIC ACID IN MILK.—In estimating boric acid in milk by Thomson's method, Liverseege and Bagnall (*ANALYST*, 1924, **49**, 133) found that, in presence of excess

of alkali, boric acid is not volatile at a red heat. This appears to suggest that so long as the percentage of fat in the substance is below a certain figure, no appreciable loss will result in the process of ignition. In the method detailed (ANALYST, 1923, 48, 416), the possibility of loss through ignition of fats and oils is overcome by extracting the fat with ether and igniting the defatted residue. I have found by experience that the fat portion extracted with ether contains a considerable amount of boric acid, so that it is always necessary carefully to re-extract the boric acid from the mixture of fat and ether by means of an aqueous solution of caustic soda and to add the latter to the bulk used in the determination.

SUMMARY.—From the foregoing historical notes it will be observed that the determination of boron compounds has passed through several interesting phases. In dealing with animal and vegetable products, the boron compounds can only be determined after all likely sources of interference have been eliminated or rendered inactive. Only in the case of a few definite classes of substances, such as butter and margarine, can actual separation of the organic matter, etc., be dispensed with, and a comprehensive method of general application, such as that already mentioned (ANALYST, 1923, 48, 416), is necessarily somewhat laborious. The main points to be observed in determining boron compounds in organic compounds are as follows:

- (1) Separation of the boron compounds from the organic matter.
- (2) Eliminating phosphates and carbonic acid, and
- (3) Choice of suitable indicators and media for the titration.

The first of these has for long been a source of worry to chemists; yet, curiously enough, it has hitherto not been very fully investigated. The present investigation was therefore carried out with a view to discover *inter alia* how the separation of boron compounds from the organic matter in animal and vegetable products can most readily be accomplished.

(To be continued.)

A New Reagent for the Colorimetric Determination of Minute Amounts of Copper.

By THOMAS CALLAN, M.Sc., Ph.D., F.I.C., AND
J. A. RUSSELL HENDERSON, D.Sc.

THE literature dealing with the colorimetric determination of copper in water, foodstuffs and allied materials is a large one. Yoe (*Photometric Chemical Analysis*, Part I.—*Colorimetry*) gives a bibliography of some sixty references covering the years 1866 to 1926. Numerous reagents have been suggested for this determination, but the two which appear to have found most favour are potassium ferrocyanide and sodium ethyl xanthate, which give a pink and a yellow colour respectively with

copper. While the xanthate method is more sensitive than the ferrocyanide, the yellow colour is not a particularly good one for matching purposes, especially when the amount of copper is very small.

Quite recently Clarke and Jones (ANALYST, 1929, 54, 333) have put forward a method in which dimethylglyoxime is used in the presence of an oxidising agent. We find, however, that, whilst this method gives very good results, provided the conditions laid down by the authors are strictly adhered to, slight variations in the hydrogen ion concentration of the solution under examination have a marked effect on the intensity of the colour. Despite, therefore, the numerous reagents which have been put forward, a really satisfactory reagent still remains to be discovered.

Some time ago we found that sodium diethyldithiocarbamate,* $(C_2H_5)_2N.CSSNa$, which is a white crystalline substance readily soluble in water, and to a less extent in alcohol, and which is easily prepared by the action of carbon disulphide on diethylamine in the presence of alkali, gives a brown precipitate of the normal copper salt of diethyldithiocarbamic acid with solutions containing copper, and appeared to have distinct possibilities as a reagent for the determination of minute amounts of copper. This reaction has therefore been fully investigated.

The following table shows the results obtained with the new reagent (0.1 per cent. aqueous solution), compared with potassium ferrocyanide and sodium ethyl xanthate, with solutions of copper salts containing from 0.1 to 1 part per million of copper.

TABLE I.

Reagent.	1. 100 ml. distilled water.	2. 0.00001 grm. Cu in 100 ml. = 0.1 pt/million.	3. 0.00002 grm. Cu in 100 ml. = 0.2 pt/million.	4. 0.00005 grm. Cu in 100 ml. = 0.5 pt/million.	5. 0.0001 grm. Cu in 100 ml. = 1 pt/million.
Potassium ferrocyanide.	Slight darken- ing due to ferrocyanide.	Slightly deeper than 1 but no pink colour.	Slightly deeper than 2. Very faint pink colour.	Definitely pink in colour.	Considerably deeper in colour than 4.
Sodium ethyl xanthate.	No change.	Very slightly yellow.	Slightly deeper than 2. Yellow colour quite definite.	Proportional increase in depth of yellow colour.	
Sodium diethyl dithiocarbamate.	No change.	Very definite golden brown colour.	Deeper golden brown.	Still deeper golden brown.	Slightly cloudy and very deep golden brown colour. Appears to be about the upper limit to which it is de- sirable to go.

These results show (1) that sodium diethyldithiocarbamate is a more sensitive reagent than either potassium ferrocyanide or sodium ethyl xanthate, and (2) that the gradation in depth of colour with increasing amounts of copper is excellent.

We have found that the colour given with the new reagent is easily matched against the colours given by known copper standards, and that as little as one part

* Obtainable from British Drug Houses, Ltd., Graham St., City Road, London, N.1.

of copper per 100 million parts of distilled water gives a very faint colour, whilst the colour with one part per 50 million is quite definite.

The colour which the new reagent gives with copper is the same in neutral, acid or alkaline solution; cyanides inhibit the reaction, owing to the formation of a cuprocyanide which does not give the reactions for copper ions.

The reactions of sodium diethyldithiocarbamate with the more common metals have been investigated, and the results are given in Table II, where Column A gives the result of adding a concentrated solution of sodium diethyldithiocarbamate (about 20 per cent.) to a fairly strong solution of the metallic salt (5–10 per cent.), whilst column B shows the result of adding a 0.1 per cent. solution of the dithiocarbamate to dilute solutions of the metallic salts containing about 1 to 20 parts per million of the metal.

TABLE II.

	A.	B.
Aluminium	White curdy ppt.	White opalescence
Antimony	Yellowish white ppt.	White turbidity
Barium	Slight white ppt.	Clear
Bismuth	White curdy ppt.	White turbidity
Cadmium	Creamy white ppt.	White turbidity
Calcium	Slight white ppt.	Clear
Chromium	Dark green ppt.	Very faint turbidity
Cobalt	Greenish brown ppt.	Yellow coloration
Iron (ferrous)	Light brown ppt.	Brown colour
Iron (ferric)	Very dark brown ppt.	Deep brown colour
Lead	White curdy ppt.	White turbidity
Magnesium	Slight white ppt.	Clear
Manganese	Dirty yellow ppt.	Very faint turbidity
Mercury(ous)	White ppt.	Very faint turbidity
Mercury(ic)	Yellowish white ppt.	White turbidity
Nickel	Yellow green ppt.	Yellow white turbidity
Silver	Pale yellow ppt.	Very faint turbidity
Tin (stannous)	Buff ppt.	White turbidity
Tin (stannic)	Pale buff ppt.	—
Titanium	Dirty yellowish ppt.	Yellowish white turbidity
Uranium	Bright orange ppt.	Golden yellow colour
Zinc	White curdy ppt.	White turbidity

The effects of iron, lead and zinc on the copper reaction have been more fully investigated.

A. IRON.—Iron gives a brown colour which interferes with the copper colour. Iron, however, can be completely removed without loss of copper by adding excess of ammonia to the solution and filtering off the ferric hydroxide, the copper being determined in the filtrate.

B. LEAD.—Lead, if present in appreciable amount, gives a white turbidity in dilute neutral, acid or ammoniacal solution, the turbidity interfering with the copper reaction. If, however, a few drops of 10 per cent. ferric chloride solution are added to the lead-copper solution, and the solution boiled, made ammoniacal, and the precipitate filtered off, the whole of the lead is removed without loss of copper, which can then be determined in the filtrate.

C. ZINC.—Zinc in neutral solution gives a white turbidity. When, however, the zinc present does not exceed 0.1 grm. per 100 ml. (that is, 1000 times the maximum

amount of copper for which the method is applicable) the addition of 2–5 ml. of 0.880 ammonia per 100 ml. prevents its interference with the copper reaction, provided that the amount of reagent recommended is not largely exceeded.

METHOD OF DETERMINATION.—The following procedure has been found to be generally applicable:—The solution containing copper, freed from other metals when necessary, is made up to a suitable volume in a measuring flask, and an aliquot portion is pipetted into a 100 ml. Nessler cylinder, diluted with water, made slightly ammoniacal (or strongly ammoniacal if zinc is present), 10 ml. of a 0.1 per cent. solution of the reagent added, and the whole diluted to 100 ml. and well mixed.

Standard comparison solutions are prepared in the same way with suitable volumes of a copper solution containing 0.00001 grm. of copper per ml. This copper solution is prepared by dissolving 0.3928 grm. of pure recrystallised copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) in a litre of water (1 ml. = 0.0001 grm. of copper), and further diluting 25 ml. of this solution to 250 ml. in a measuring flask (1 ml. = 0.00001 grm. copper). The amount of copper in the solution to be tested should not exceed 0.0001 grm. per 100 ml. (10 ml. of standard copper solution), as above this concentration the depth of colour becomes too dark for satisfactory matching.

The colour is quite stable for at least an hour, even when copper is present much in excess of the limit at which matching is possible, thus affording ample time for matching colorimetrically against standard copper solutions, but after this time a cloudiness develops, owing to the oxidation of the reagent.

An aqueous solution of sodium diethyldithiocarbamate keeps fairly well, a 0.1 per cent. solution in an amber-coloured bottle remaining apparently unchanged after several weeks.

An extended use of the reagent over a considerable period has confirmed its value and superiority over the more usual reagents. It was found to be of particular value in the course of a prolonged investigation of methods for the determination of copper in dyestuffs and rubber-proofed fabrics—a matter of no little importance in the rubber industry—and also in the determination of minute amounts of copper in acids, alkalis, etc.

We are indebted to Mr. H. E. Jones, of Messrs. Brunner, Mond & Co., Ltd., who has applied the new reagent to the determination of minute quantities of copper in caustic soda, for the following list of results, obtained in each case on 5 grms. of material:

SAMPLE A.		SAMPLE B.		
Copper added. Grm.	Copper found. Grm.	Copper added. Grm.	Copper found. Grm.	Added copper found. Grm.
Nil	Nil	Nil	0.00014	—
0.00001	0.000008	Nil	0.00015	—
0.00002	0.000019	0.00007	0.00022	0.00007
0.00003	0.000029	*0.00015	0.00029	0.00014
0.00004	0.000040	*0.00010	0.00025	0.00010
0.00005	0.000049	*0.00015	0.00030	0.00015

In the cases marked * the amount of copper added was unknown to the analyst who made the determination.

In conclusion, we have to thank the British Dyestuffs Corporation, Ltd., in whose Central Analytical Laboratory the work was carried out, for their kind permission to publish the results of this investigation.

The Electrolytic Separation of Lead and Bismuth with Controlled Potential.

By ELLA M. COLLIN, B.Sc., A.I.C.

IN the methods hitherto described for the purely electrolytic separation of lead and bismuth (H. Sand, *J. Chem. Soc.*, 1907, **91**, 385; Lassieur, *Electroanalyse Rapide*, Paris, 1927, p. 108) the bismuth is first deposited at a controlled cathode potential, a reducing agent being added to the solution, and the lead is then deposited as metal. The reducing agents used by Sand were glucose and tartaric acid, but Lassieur substituted hydroxylamine hydrochloride. The deposition of lead as metal on the cathode is not free from objections, owing to its great tendency to oxidation on drying, and also to its deleterious effect on the platinum electrode.

The method given here is a modification of that given by Sand (*loc. cit.*), hydrazine hydrate being used as the reducing agent. This has the great advantage that it is easily destroyed, thus enabling the lead to be deposited as peroxide on the anode after the separation of the bismuth.

It is well known that, owing to the tenacity with which water is retained by lead peroxide, an empirical factor, which depends to some extent on the conditions of deposition and drying, must be employed for the calculation of PbO_2 to Pb. (H. Sand, *Chem. News*, 1909, **100**, 269; R. O. Smith, *J. Amer. Chem. Soc.*, 1905, **27**, 1287; A. Fischer, *Z. Elektrochem.*, 1904, **10**, 945.) Several experiments were carried out with a view to finding such a factor for the amount of lead deposited as peroxide.

All the experimental work in this paper was done with a rotating electrode, and with the use of the apparatus designed by Sand and described by him (ANALYST, 1929, 275).

The solution, containing the lead as nitrate, is treated with a strong solution (about 50 per cent.) of sodium hydroxide, just sufficient to redissolve the precipitate, and then acidified with nitric acid, 20 c.c. in excess being added; the total volume is about 120 c.c. It is electrolysed at a temperature of 90° – 95° C., with a current of 6–6½ amps. In each experiment, before disconnecting, a small quantity of the solution is withdrawn, made alkaline, and tested with hydrogen sulphide, to ensure that the deposition of the lead is complete. The deposit is dried by dipping the electrode in alcohol and then ether and holding it at some distance above a Bunsen flame.

Amount of lead taken. Grm.	Weight of PbO_2 found. Grm.	Factor PbO_2 :Pb.
0.1000	0.1153	0.8673
0.1000	0.1156	0.8651
0.2000	0.2318	0.8628
0.3000	0.3467	0.8653
0.4030	0.4640	0.8620
0.5072	0.5895	0.8604

On the basis of these results the factors taken for the calculation of PbO_2 to Pb in the subsequent determinations are as follows:

Up to 0.1 grm. Pb	0.8660
From 0.1 grm. Pb to 0.4 grm. ..	0.8635
From 0.4 grm. Pb to 0.5 grm. ..	0.8605

These factors agree closely with those found by Sand, Smith and Fischer.

THE SEPARATION OF LEAD AND BISMUTH.—To the solution of the two metals, present as nitrates in a volume of about 60 c.c., is added an excess of 3 c.c. of nitric acid, and 4 or 5 drops of a 50 per cent. solution of hydrazine hydrate. The electrolytic deposition of the bismuth is carried out at a temperature of 80° – 85° C., according to the method described by Sand (*J. Chem. Soc.*, 1907, 91, 373), but with a *N*/100 nitric acid quinhydrone auxiliary electrode, the initial current being 1.3 amps. at a cathode potential of -0.45 volt (referred to the quinhydrone electrode), which is reduced by the end of the electrolysis to practically zero at a potential of -0.6 volt. After the removal of the bismuth a strong solution (about 50 per cent.) of caustic soda is added to the electrolyte while it is still hot, until the precipitated lead hydroxide is just redissolved. Sodium peroxide is then added in small quantities, and the solution heated until all brown fumes and precipitate have cleared. The addition of the sodium peroxide is continued until the last portion produces no further brown fumes. The solution is heated gently for about five minutes, and then cooled somewhat. It is then acidified with concentrated nitric acid, with the addition of 20 c.c. in excess, the total volume by this time being about 120 c.c. The solution is electrolysed, as previously described, with a current of 6–6.5 amps.

RESULTS.

Taken.		Found.		Time taken for electrolysis. Minutes.
	Grm.	PbO_2 Grm.	Grm.	
Bi:	0.1000		Bi: 0.0997	7
Pb:	0.4000	0.4627	Pb: 0.3995	12
Bi:	0.3882		Bi: 0.3875	12
Pb:	0.2000	0.2313	Pb: 0.1997	15
Bi:	0.2103		Bi: 0.2105	10
Pb:	0.4325	0.5005	Pb: 0.4322	18
Bi:	0.2000		Bi: 0.1996	10
Pb:	0.2000	0.2305	Pb: 0.1990	12
(Trace of lead found in electrolyte.)				
Bi:	0.1000		Bi: 0.0998	8
Pb:	0.1000	0.1155	Pb: 0.1000	12
Bi:	0.4000		Bi: 0.4010	15
Pb:	0.4000	0.4622	Pb: 0.3991	15

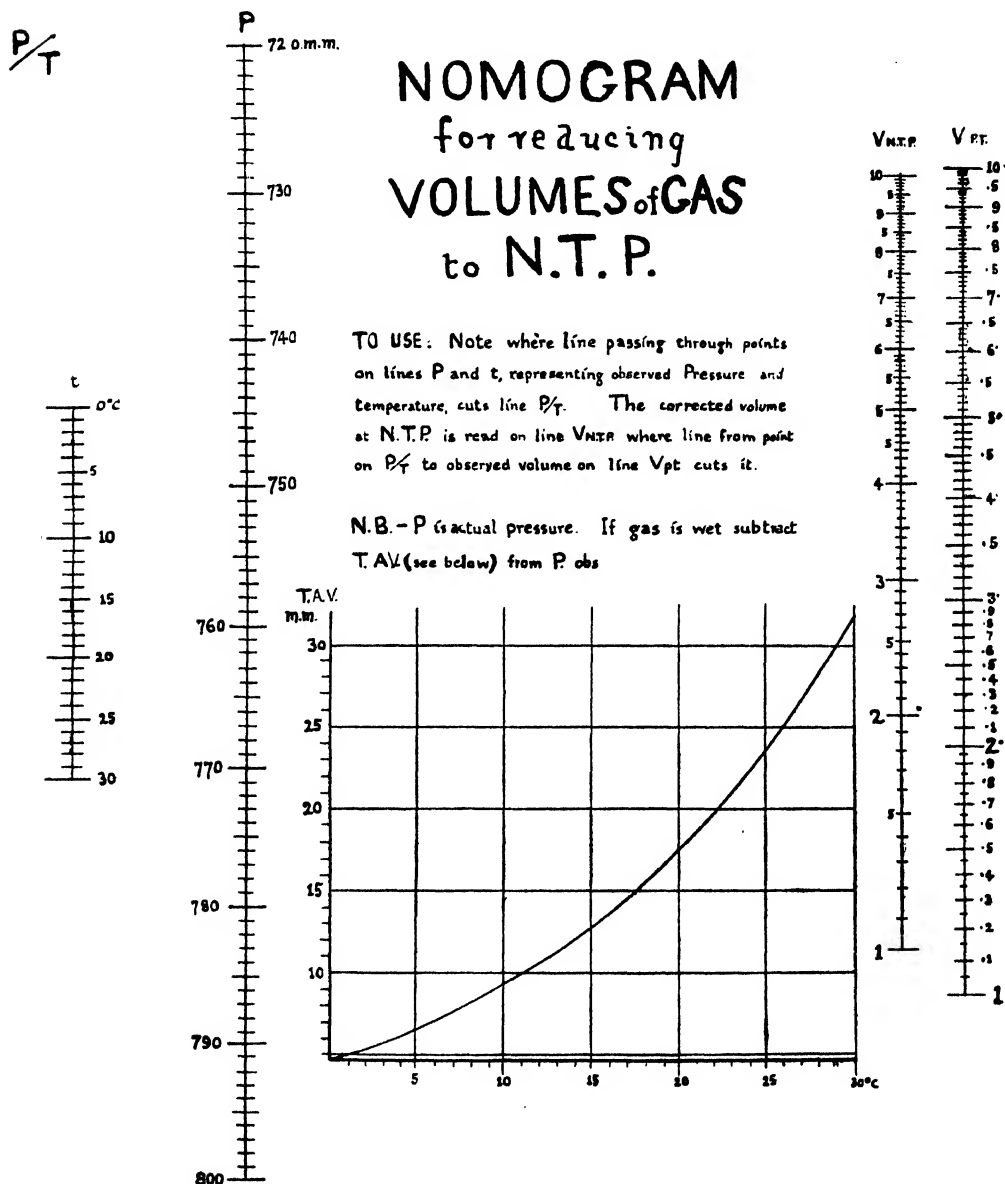
In conclusion, I wish to express my thanks to Dr. H. Sand for his suggestions and interest during the course of this work.

THE SIR JOHN CASS TECHNICAL INSTITUTE,
LONDON, E.C.3.

A Nomogram for Converting Observed Volumes of Gas to Normal Temperature and Pressure.

By J. H. COSTE, F.I.C.

(Demonstrated at the Meeting, October 2, 1929.)



THE attached nomogram has been drawn to enable necessary corrections to standard temperature and pressure to be made over a reasonable range of variations of temperature and pressure with sufficient accuracy for many purposes.

The four graduated lines, P , t , V_{pt} and V_{NTP} , represent the logarithms of the natural numbers inscribed against them, and are placed at such distances apart as are appropriate to the scales. The manner of using the nomogram is inscribed thereon. Exact alignment on the scales and pivoting on the ungraduated line, P/T , is best secured by cutting a strip of transparent celluloid with a V-notch at one end and a line drawn with a point (a gramophone needle is convenient) along from the point of the V to the other end of the strip. This can be aligned on the relevant points on P and t and slid along until a pin held in the point of the V-notch touches P/t , in which it is stuck. The scratched line of the slip can then be brought to coincide with the observed volume on V_{pt} and the corrected volume read off on V_{NTP} .

Examples:—

- I. 8.31 c.c. of gas at 17° and 730 mm. (dry) = 7.48 c.c. at N.T.P. (Five figure logarithms give 7.51 c.c.)
- II. 11.3 c.c. of gas at 4° and 777 mm. (moist) = 11.3 c.c. at N.T.P. (Five figure logarithms give 11.30 c.c.)

This nomogram has been in use for some years. I notice that one has recently been described by O. Liesche (*Chem. Fabr.*, 1928, 583-4, 595-7, 621-3).

DISCUSSION.

Mr. G. N. HUNTLY stated that he had found Dr. Farmer's gas calculator* for reducing gas volumes very useful. This gave, not the corrected volume, but the factor for reducing to N.T.P. by a single multiplication. Its accuracy was 1 in 5000.

* Published by Baird & Tatlock (London) Ltd.

Official Appointments.

THE Minister of Health has confirmed the following appointments:

MR. A. E. JOHNSON, B.Sc., F.I.C., as Public Analyst for the County Borough of Wolverhampton, to date from December 10, 1929; also as Public Analyst for Newcastle-under-Lyme, to date from December 1, 1929. Mr. E. Victor Jones, F.I.C., relinquishes these appointments on the respective dates mentioned.

MR. D. T. LUCKE, B.Sc., A.I.C., as Additional Public Analyst for the County Borough of Southend-on-Sea.

Notes.

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

ROUTINE DETERMINATION OF SALT IN BUTTER AND MARGARINE.

THE method published by Steuart (ANALYST, 1928, 53, 212) was examined and found to be amenable to further simplification by the use of 10 c.c. of hot water instead of acetone. The following method is proposed for rapid routine determinations:—Weigh 3 grms. of the sample on a large cigarette paper, and drop paper and sample into a 150 c.c. conical flask. Add 10 c.c. of boiling distilled water, shake well, and titrate with 0.1 *N* silver nitrate solution, using chromate indicator; towards the end-point, close the flask and shake well, as in Steuart's method.

This method gives results which are the same as those obtained by the acetone method, and are in substantial agreement with results obtained by the standard method, consisting in drying the butter or margarine, extracting the fat with petroleum spirit, extracting the solids-not-fat with water, and filtering and titrating the aqueous extract as usual. The following results will give an idea of the agreement obtained, and it will be seen that the differences are not of such an order as to play any part in the commercial judgment of butter or margarine:

Sample No.	Salt by standard method.	Salt by rapid hot water method.
	Per Cent.	Per Cent.
1	4.80	4.58
2	2.59	2.65
3	2.20	2.04
4	1.63	1.67
5	1.42	1.46
6	0.95	0.92
7	0.59	0.65
8	0.31	0.37

PAUL ARUP.

BUTTER TESTING STATION,
DUBLIN.

EXAMINATION OF GOATS' MILK FOR UNBOILED MILK.

IN testing whether the goats' milk sold in Gibraltar complies with the Regulation that it shall have been boiled (*cf.* ANALYST, 1929, 593) the following method of estimating small amounts of unboiled milk is used. The milk should be fresh, and it is not practicable to estimate more than 30 per cent. of unboiled milk; when there is more than this the results are returned as indicating wholly unboiled milk.

The colorations given by the enzymes in milk (which are destroyed on heating

the milk to 80° C.) with various reagents in the presence of hydrogen peroxide are as follows:—Ortol, deep red; paradiaminobenzene, indigo-violet; hydroquinone, deep pink; guaiacol, brick red; guaiacum, blue. The results of tests which I made indicated that ortol is the most sensitive of these reagents, with paradiaminobenzene next. With either of these as little as 2·5 per cent. of unboiled milk could be detected with certainty, but with guaiacol 30 per cent. could escape detection.

ORTOL METHOD.—The test is as follows:—Place 5 c.c. of the milk in a test tube, and add 1 drop of 10 per cent. hydrogen peroxide (90 vol.), and then 1 c.c. of a freshly made 1 per cent. aqueous solution of ortol. (If less than 10 per cent. of unboiled milk is to be estimated, the hydrogen peroxide is reduced to 2 drops of a 1 per cent. solution.)

The colour is formed almost at once if unboiled milk is present, whereas for wholly boiled milk only a slight pink is discernible after some time. In the presence of 2·5 per cent. of unboiled milk the pinkish colour is formed at once.

The colour formed is compared with those obtained with known percentages of unboiled milk, standards and tests being made at the same time.

The Paradiaminobenzene method, which I use as a confirmatory test, is carried out in a similar manner, the strengths used being as follows:—Paradiaminobenzene, 0·25 per cent. aqueous solution; hydrogen peroxide, 1 drop (90 vol. equally diluted); milk, 5 c.c. Readings should be taken after one minute and not later than two minutes after mixing. Wholly boiled milk develops a bluish tint from three to five minutes.

I was driven to make these experiments because the Pasteur Institute at Tangier differed from my findings of 10 per cent. of unboiled milk in a prosecution case last year. The Pasteur Institute used guaiacol, which, as I found experimentally, does not detect 30 per cent., or even more, of unboiled milk.

A. G. HOLBOROW.

CITY COUNCIL LABORATORIES,
GIBRALTAR.

DISTRIBUTION OF ARSENIC IN THE BODY IN A FATAL CASE OF POISONING BY HYDROGEN ARSENIDE.

IN connection with a fatal case of arsenical poisoning which occurred in Westland, New Zealand, in 1926, it became necessary, owing to legal issues involved, to investigate the cause of death more fully than usual. As the distribution of arsenic in the body in cases of gaseous arsenical poisoning appears to have been recorded on comparatively few occasions, a brief account of this case should be of interest.

The liberation of hydrogen arsenide resulted from the treatment of zinc slimes by sulphuric acid during the recovery of gold by the cyanide process. No special precautions were taken to carry off the gases evolved during the process, and the conditions were such that it was probable that gases evolved would be inhaled by the operator. The plant had been in operation for a considerable time, when the operator was suddenly taken ill. Two days later he obtained medical advice, when arsenical or similar poisoning was diagnosed. Treatment on these lines was given, but death occurred after 9 days, the immediate cause of death being complete suppression of the urine.

The organs referred to below were submitted to me, as district Government Analyst, for chemical analysis, with a request for a full examination, as important issues were involved. Arsenic was detected by the Reinsch test, and quantitative

determinations were then made on fairly large amounts of each organ. Destruction of organic matter was effected by digestion with nitric and sulphuric acids, the former being added in small quantities till the liquid ceased to char (modified Gautier's process). The liquid, freed from nitric acid by further heating, was then suitably diluted. The arsenic present was determined by the electrolytic Marsh process, with the use of a platinum anode and a lead cathode (see Sand and Hackford, *J. Chem. Soc.*, 1904, **58**, 1018; and Monier-Williams, *ANALYST*, 1923, **48**, 112, 262).

Blank determinations with the reagents used gave negative results. The distribution of arsenic was as under:

Organ.					Arsenic present (calculated as As). Mgrms. per kilo.
Brain	1.40; 1.0
Lungs	2.59; 2.3
Stomach and contents	0.10; 0.3
Spleen	0.48; 2.2
Kidney	0.36; 1.3
Liver	6.90; 4.4.

I expressed the opinion that the distribution would be consistent with gaseous arsenical poisoning, and a verdict was given on these lines.

At the time of the accident roasted concentrates were being treated, and an unusual white precipitate had been observed in the zinc precipitating boxes, which the operator thought was cyanide of zinc. Subsequent to the accident an investigation was made by the company, and it was found that the roasted concentrates contained 1.4 per cent. of arsenic (calculated as element). The white precipitate in the boxes contained 8.0 per cent. of arsenic (element), also lime and zinc. The percentages of lime and zinc, and the nature of the combination, whether arsenate or arsenite, were not determined. A white deposit, similar in appearance, which had collected in the pipe leading from the cyaniding tank to the zinc boxes, consisted almost entirely of carbonate and arsenate of lime, the percentage of arsenic present (calculated as element) being 9.85. The lime in both precipitates had, no doubt, been derived from lime used to counteract possible acidity of the concentrates. It was found that hydrogen arsenide was evolved when these precipitates were treated with sulphuric acid in the presence of zinc. The presence of hydrogen arsenide being accounted for, no further chemical investigation was carried out by the company.

The danger attached to the process was successfully overcome by the provision of adequate means of removing the evolved gases from the sulphuric acid vat. The vat was closely covered, and the gases conveyed to a flue by a current of compressed air. Hydrochloric acid was eventually substituted for sulphuric acid, thus avoiding the necessity for stirring.

I wish to thank Dr. J. S. Maclaurin, Dominion Analyst, Wellington, for permission to publish these results.

F. J. T. GRIGG.

GOVERNMENT LABORATORY,
CHRISTCHURCH, NEW ZEALAND.

Notes from the Reports of Public Analysts.

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY AND COUNTY OF KINGSTON-UPON-HULL.

ANNUAL REPORT OF THE PUBLIC ANALYST AND BACTERIOLOGIST FOR THE YEAR 1928.

DURING the year the number of samples and specimens examined was 7479. Of these, 1666 were food and drugs samples; comprising 808 official, 427 informal, and 431 miscellaneous samples; 74 of these were suspicious, and 54 (3·8 per cent.) were adulterated. The lower percentage of adulterated and suspicious samples, as compared with the year 1927, was largely due to the more definite position regarding the illegality or otherwise of the use of preservatives.

DIRT IN MILK.—Only 6 of the 579 samples of milk examined contained unwarranted amounts of dirty sediment; this is the lowest figure recorded for some years.

BONDON CHEESE.—A sample of so-called *Bondon Cheese* was reported as adulterated, since it was a skimmed-milk cheese containing only 5·3 per cent. of fat. The opinions of traders as to the method of manufacture and the composition of this cheese are conflicting, but it can scarcely be denied that Neufchâtel Bondon Cheese was originally made, and is to-day made, from whole milk. Therefore such cheese should be prepared as in Neufchâtel, France, and should contain at least 20 to 25 per cent. of fat.

ICE-CREAM.—Twenty samples were examined chemically during the year, and all were found to consist of sweetened farinaceous mixtures, with milk or milk and water as a basis. The amount of milk-fat present in the samples varied from 1·0 to 4·4 per cent., with an average of 2·5 per cent. No fewer than 14 out of the 20 samples contained less than 3·0 per cent. of fat, and nine less than 2·5 per cent. All the samples failed to approach the standard of 6 or 8 per cent. milk-fat suggested by the trade and other bodies. These confections were therefore not properly named "ice-cream," which term should certainly be restricted to a product containing some addition of cream to the milk (not milk and water) used in making them. All the 20 samples were free from preservatives and deleterious metallic contamination.

Twenty-nine samples were examined bacteriologically, and 13 were found to be more or less contaminated with objectionable organisms, due to unclean utensils and methods of manufacture. These 13 samples contained from 140,000 to 16,000,000 organisms per c.c., with evidence of the presence of the *Bacillus coli* in one-thousandth to one ten-thousandth of a cubic centimetre of the melted samples. Ice-cream of satisfactory purity ought to contain no *Bacillus coli* in less than 0·1 c.c. Inspections of the premises where ice-cream is manufactured have been made during the year by the sampling officer, and, where necessary, representations have been made to the owners regarding improved methods and plant.

COFFEE AND CHICORY EXTRACT (POWDER).—A sample of this new product had the characteristics to be expected in a dried extract, in powder or "scale"

form, of the soluble substances in coffee and chicory; it contained about 4 per cent. of caffeine. The label, however, was considered unsatisfactory, in that it did not specify the nature of the contents, but bore the words: "—Coffee. Sold as a mixture of Coffee and Chicory." On the attention of the manufacturers being called to the matter, they agreed to alter the wording to read: "A desiccated extract of Coffee and Chicory."

CONFECTIONERY (SWEETS).—Two of the 24 samples of cheap sweets (chocolates, candy, nougat, pastilles, etc.) purchased in the vicinity of the Fair Ground, contained 850 and 1640 parts per million of sulphur dioxide. Action was taken in connection with the second (formal) sample, and the vendor was fined £1.

MUSTARD AND PREPARED MUSTARD.—Ten samples of mustard and 5 of prepared mustard were examined during the year. Of the 10 mustard samples, 6 were genuine, while 2 contained a farinaceous addition; in one sample 20 per cent. of wheat-flour, and in the other 10 per cent. of maize-flour (cornflour). These were also regarded as genuine, since each was labelled as a "mustard compound," and sold as a mixed article. Two other samples (adulterated and of suspicious character) contained 2 per cent. of maize-flour, with turmeric.

The five samples of *prepared mustard* are the first to be examined in the City Laboratory. These preparations, frequently known as "French" or "German" mustard, consist generally of mustard which has been mixed with vinegar and probably with water in addition, together with salt, and sometimes spices. Provided such articles contain a due amount of mustard—the main ingredient in a satisfactory preparation—and no "filling" ingredient without disclosure, they may be regarded as satisfactory in nature. Four of the 5 samples passed these requirements, and showed an average content of about 65 per cent. of water, including 1–4 per cent. of the acetic acid of vinegar. The remaining sample (an English preparation) showed evidence of an appreciable proportion of wheat flour. There was no disclosure by label in this instance, and the sample was reported as of suspicious character.

PEPPER AND PEPPER MIXTURES.—Nineteen samples of this condiment, many of them being sold in 1d. and 2d. cartons or tins, were examined. Seventeen of the samples were sold as pepper, and 3 of these were reported as of suspicious character; two contained about 1 per cent. of maize flour with turmeric colouring-matter, while the other sample contained the same amount of a mixture of maize-flour and arrowroot with added colouring matter. Fourteen samples consisted of the genuine ground spice, though some were coloured with turmeric. The two remaining samples were labelled "Prepared Pepper" and "Compound Pepper," and also bore the words on the containers, "Sold as a mixed article." Each consisted of equal weights of pepper and a foreign substance, in one instance rice-flour and in the other, maize-flour. The labels protected the vendors, though why it is supposed that the public likes these "fillings," which are useless in pepper, is difficult to understand. It is unsatisfactory that the word "pepper" in such cases is allowable in law.

ICE.—Ice used for putting into summer drinks should be bacteriologically pure, and should always be washed in clean water before use. Two samples of ice examined showed somewhat unsatisfactory results, since they contained four to eight thousand organisms per c.c. and *Bacillus coli* in 0.1 c.c. and in 1 c.c. Representations were made to the proprietors of the cafés concerned.

SHRIMPS.—Two samples of boiled shrimps, examined bacteriologically, proved to be free from organisms of the food-poisoning (*Salmonella*) group, and of the typhoid-paratyphoid group, but the *Bacillus coli communis* was present in one

sample to the extent of about 40 per fish, and these shrimps were regarded as unsatisfactory. A further sample from the same source proved to be of satisfactory purity.

SUNLIGHT (ULTRA-VIOLET RAYS) OBSERVATIONS.—These observations have been continued throughout the year, and, during most of this period, records have been taken at two stations. The central area was represented, as before, by an apparatus placed on the roof of the Telephone Exchange in Mytongate, while a suburban site was chosen in February at Pearson Park (roof of greenhouse). The "units of fading" of the standard coloured solution used are a measure of the ultra-violet rays in the sunlight reaching any given area. The maximum and minimum daily average figures for the two Hull stations, together with those of certain other towns, are given in the following table. The daily "units of fading" are calculated from the total of each separate month's records:—

UNITS OF FADING. DAILY AVERAGE THROUGHOUT THE MONTHS MENTIONED.

	Maximum.	Minimum.		Maximum.	Minimum.
Hull (Central) ..	2.8 (July)	0.2 (Dec.)	London Kingsway	6.8 (July)	0.2 (Dec.)
" (Suburban) ..	3.2 (July)	0.2 (Dec.)	" Hampstead	15.8 (July)	0.5 (Dec.)
Cardiff ..	5.2 (July)	0.9 (Dec.)	Lowestoft ..	13.0 (Aug.)	1.5 (Jan.)
Huddersfield ..	3.9 (July)	0.3 (Jan.)	Stirling ..	3.4 (June)	0.5 (Jan.)

STAINED FABRIC.—A piece of white fabric, said to have been stained by boiling in water in a gas-boiler, was submitted for examination. The lining of these boilers has previously been shown to consist of an alloy of lead and tin, and the stains on the cloth contained a material amount of the first-named metal.

A. R. TANKARD.

Legal Notes.

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

PEPPER COMPOUND.

ON August 20, a shopkeeper was summoned at Sheffield for selling a mixture which was not the pepper compound demanded.

An inspector had bought from the defendant's shop cartons, labelled "Penny Pepper," which were being sold as "Pepper Compound." On analysis, the mixture was reported to consist of 50 per cent. of pure pepper and 50 per cent. of rice starch.

Mr. A. Neal, for the defence, said that the wholesale merchants would be prepared to justify their position if their warranty was accepted. Their invoice, bearing a guarantee that the goods were of the nature, substance and quality described, was produced.

The magistrates accepted the warranty and dismissed the case.

On October 16, the summons against the wholesale merchants who had given the warranty was heard.

Mr. W. A. Williams, for the prosecution, contended that the articles referred to in the warranty were not of the nature described. If a compound constituted

a fraud upon the public, the fact that it was described as a compound was no protection. The purchaser would imagine that he was getting something similar to pepper in that part of the compound which was not pepper.

Mr. John Evans, F.I.C., Public Analyst for Sheffield, who was called in support of his certificate, said that he had detected traces of other substances, such as pea meal and capsicum, in the compound, but that he had regarded them as mere impurities.

Mr. S. E. Melling, Public Analyst for the County of Cheshire, called in support of the City Analyst's Certificate, said that the amount of rice in the mixture was excessive, but agreed that he could not fix a standard.

Mr. F. W. Scorah, solicitor for the defence, submitted that the Bench had power to fix a standard on the evidence, and in that case they could not say that the amount of rice was excessive.

Mr. E. J. Parry, F.I.C., said that there was no legal standard for pepper compound. He accepted the evidence that there was 50 per cent. of rice-flour in the compound, but said that the rice-flour was impregnated with capsicine, which was 500 to 1000 times as pungent as pepper, and found other spice extracts. He considered that the compound had been prepared by the most reasonable method.

The Chairman of the Bench said that he did not understand why, when other substances had been detected, they were not mentioned in the Analyst's certificate. The Bench were of opinion that a case had not been made out, and dismissed the summons.

SULPHUR DIOXIDE IN GROUND GINGER.

ON September 25, a co-operative society was summoned at Eccleshall (Staffs.) for selling ground ginger containing 0.0416 per cent. of sulphur dioxide, and a Lancashire wholesale co-operative society was summoned for giving a false warranty in respect of this ginger.

For the defence it was stated that the ginger had been sold by the wholesale co-operative society, as received from their depôt in India, where there were no restrictions on the use of sulphur dioxide for ginger. The preservative was used to protect the ginger root from the effects of damp. The defendants undertook to do their best not to put any more such ginger on the market.

The case against the first defendants was dismissed, and the wholesale co-operative society was fined £3, with £5 1s. 6d. costs.

REMOVAL OF ORIGIN MARKS FROM EGGS. USE OF ULTRA-VIOLET RAYS IN COURT.

ON October 8, a tradesman was summoned at Glasgow for having sold, as fresh country eggs, imported eggs from which the mark of origin had been removed, the allegation being that an acid had been used for this purpose.

Mr. T. Cockburn, Chief Assistant in the Glasgow Corporation Laboratory, supplemented this evidence by making an actual demonstration in Court with an ultra-violet light apparatus. He showed how eggs could be examined by means of this apparatus, and demonstrated that the area of corrosion by acid showed a deep purple colour, as compared with the light colour of the remainder of the shell. He then placed under the rays the eggs which formed the subject of the summons.

The Stipendiary Magistrate said that he was satisfied that there had been tampering with the eggs, and imposed a fine of £5, with £3 costs.

Report of the Government Chemist upon the Work of the Government Laboratory

FOR THE YEAR ENDING MARCH 31ST, 1929.*

THE chemical work of the same Government Departments as in previous years was undertaken (ANALYST, 1928, 53, 593-596), and, in addition, work has been done in connection with the Ethyl Petrol Committee, the Atmospheric Pollution Research Committee and surveys of rivers. The total number of samples examined was 499,289, an increase over the previous year of 8250. The Hydrocarbon Oils Duty involved the examination of over 12,000 samples, and there is again an increase in tobaccos for payment of drawback on exportation (74,415 samples against 44,365) owing to the increased manufacture of cigarettes for export from duty-free leaf. The discontinuance of bonded sugar refineries accounts for an increase of about 7000 sugar samples. Wine and tea samples have decreased from 99,391 to 85,703, and 41,149 to 28,896 samples, respectively.

MINISTRY OF AGRICULTURE AND FISHERIES.—*Butter*.—Five of 863 samples contained over 16 per cent. water, and 15 samples from one source had approximately 50 per cent. of foreign fat. *Margarine*.—Only 7 out of 341 contained excess water. *Cheese*.—Fifty per cent. of the samples were from cheeses prepared from whole milk, 23 from milk with three quarters to the whole of its fat, 10 from milk with half to three quarters fat, and 17 from milk with less fat. *Cream*.—Two samples of artificial cream were emulsions of whole milk and foreign fat. *Condensed milk*.—Fifteen samples of 62 were made from machine-skimmed milk, and not marked accordingly. *Sheep dips*.—Five of 67 samples were unsatisfactory.

Water and Pollution of Rivers.—Fifty-four samples of river-water, muds and effluents were examined. The diurnal variations in the quantity of dissolved oxygen in rivers have been further studied.

Fertilisers and Feeding Stuffs Act.—Of 6 fertilisers examined, one fertiliser and one superphosphate were deficient in soluble phosphoric acid, a basic slag was deficient in fine material, and 2 out of 3 shoddies in nitrogen. Of 15 feeding stuffs, 3 samples of barleymeal each contained between 25 and 40 per cent. of foreign material from tapioca root and wheat offal, 2 samples contained 2.5 and 5.0 per cent. of oats, together with small quantities of wheat and weed-seeds; a sample of meat and bone meal was deficient in phosphates, and a sample of meat meal in oil; it also contained over 4 per cent. of salt. Two samples of meat and bone

* Obtainable at Adastral House, Kingsway, W.C.2. Price 1s. 6d. net.

meal were deficient in phosphoric acid. Two laying meals were deficient in oil and protein, and one had an excess of sand; a sample of fine offals contained, in addition, 20 per cent. foreign matter, and 2 samples of feeding cake were deficient in protein. There were 2 cases of disagreement with agricultural analysts, one relating to a deficiency of nitrogen in a shoddy, and the other of protein in a feeding cake.

Miscellaneous Articles.—Fifteen samples of barley and barley meal were examined as causing illness in pigs, 2 samples of crustless cheese, to ascertain the nature of the emulsifying substance, 8 samples of rat and beetle poison, etc.

CUSTOMS AND EXCISE.—*Beer.*—The total number of samples examined was 56,236, a decrease of 1715 over the previous year. Of these, 355 consisted of malt corn, brewing sugars, exhausted grain; 207 were yeast food or miscellaneous substances; 6917 samples were for checks on assessment of duty; 7052 for checking whether dilution of beer had taken place (262 samples showed dilution had taken place, and in 20 cases it amounted to over 4 gallons of water per barrel). Tests for arsenic were made on 1238 samples, and 39 of these contained arsenic in slight excess of that allowed by the regulations. *Cider.*—Thirty-six samples of imported cider out of 188 were found to be dutiable. *Cocoa and chocolate.*—Examinations of 9501 samples from imported goods and 3425 from exported goods were made to ascertain the proportion of various ingredients present in connection with duty. *Dangerous Drugs Act.*—Six of 49 suspected drug samples contravened the Act.

Hydrocarbon Oils Duty.—The 1928 Finance Act defines "Light Oils" as "hydrocarbon oils of which not less than 50 per cent. by volume distils at a temperature not exceeding 185° C., or of which not less than 95 per cent. by volume distils at a temperature not exceeding 240° C., or which give off inflammable vapour at a temperature of less than 22·8° C. when tested in the manner prescribed by the Acts relating to petroleum." For the new duty purposes 12,055 samples were examined between 25th April, 1928, and 31st March, 1929, 9748 from imported and 2307 from exported goods. Of these, 3410 were hydrocarbon oils and 8645 goods such as enamels, lacquers, road dressings, insecticides, essential oils, etc.

Safeguarding of Industries Act.—In order to find whether the chemical was liable to duty, or whether substances bearing trade names contained dutiable ingredients, 12,288 samples were examined. *Silk.*—In connection with duty 20,872 samples were examined, 10,368 from imports, 9578 from exports, and 926 from home factories. *Spirits.*—Wood and mineral naphtha (606), pyridine (127), special denaturants (1537), exported spirits for drawback claims (2510), exported spirituous preparations (18,771) and imported spirits and spirituous preparations (13,724) were examined. *Sugar, glucose and saccharin.*—Of sugar and articles containing sugar or other sweetening matter, 68,935 samples were examined for duty or drawback assessment. *Table Water Duty.*—Of 26 mineral waters, 5 were medicinal, and 21 liable to table water duty. *Tea.*—Of 28,896 samples of tea 298 were reported against, 187 on account of foreign substances and 111 as being unfit for human consumption. *Tobacco.*—The largest number of samples are in connection with manufactured tobacco and commercial snuff for exportation on drawback; 74,415 such samples were examined, particularly for moisture, and in the case of cigarettes for paper. Offal tobaccos for repayment of duty involved examination of 42,710 samples, 29,133 of stalks, and 10,960 of offal snuff, shorts and smalls.

MINISTRY OF HEALTH.—*Preservatives Regulations.*—Examination for presence of preservatives, which are only allowed in a few specified articles to limited extent,

was carried out on 2529 samples, and 44 were reported to the Board of Customs and Excise as contravening Regulations. These included 17 samples containing sulphur dioxide either contrary to the Regulations or in excess of permitted quantities; 9 samples of tinned vegetables containing copper colouring matter; boric acid in a sample of bacon, salicylic acid in 2 fruit juices, and hydrogen peroxide in one, and boron preservative in 12 butters; no boric acid was found in margarine samples.

HOME OFFICE.—The total number of samples was 527. The yellow colour of a sample of shellac was found to be derived from added sulphide of arsenic.

FOOD AND DRUGS ACT.—Of the 27 samples of food referred under the Acts, 17 were milks, 4 butters alleged to contain foreign fat, gin and whisky with excess of water, rice with excess of mineral glaze, and ginger wine, ginger beer, and raspberry cordial containing salicylic acid. A calomel ointment was deficient in calomel, and an ammoniacal tincture of quinine in quinine. There were 4 cases of disagreement with the prosecution's analyses. Three samples of butter did not afford evidence of the presence of fat other than butter fat, and a milk alleged to be deficient in non-fatty solids contained 8.61 per cent.

D. G. H.

Medical Research Council.

TOXICITY TESTS FOR NOVARSENO BENZENE (NEOSALVARSAN).*

THE test necessary for novarsenobenzene must ensure that its toxicity does not exceed that of a standard by more than a specified amount. At present the British test is not sharply definitive, allowing an undue proportion of toxic samples to pass, the German is rather sharper, and the Japanese and American less discriminative. The proposed improved test is as follows:—The drug is dissolved in freshly re-distilled water to give a 2 per cent. solution, and the fresh solution is injected into the tail veins of the mice, which are made to fast over-night, weighed, and then given food, and the injection made 1 hour later. In the first stage 10 animals weighing 18–20 grms. are injected with 7.6 mgrm. each of the novarsenobenzene. If not more than 2 die (20 per cent. mortality) the sample is passed, and among those passing would be samples with a toxicity less than that of the standard and about 61 per cent. of those with a toxicity equal to that of the standard. The others are injected in the same dose into a further 10 mice, and the total mortality on the 20 animals so far used observed, and, if not over 40 per cent., the sample passes. A further 38 per cent. of samples of standard toxicity should pass. If more than 15 animals have been killed, the sample is rejected as exceeding the permissible toxicity. The remaining samples are injected into a further 10 mice, and those which have not killed more than 15 of the total 30 are passed and the rest rejected, so that 50 per cent. of 30 mice on a dose of 0.4 mgrm. must survive.

The test passes all samples of toxicity up to that of the standard, rejects 0.4 per cent. of those of toxicity 10 per cent. over the sample, 50 per cent. of those 20 per cent. above, and 99.6 per cent. of those 30 per cent. above. With a dose of

* Special Report No. 128, by E. H. Durham, J. H. Gaddum and J. E. Marchal. Obtainable at H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 9d. net.

0.38 mgrm., or a total dose of 7.2 mgrm., 94 per cent. of the samples 20 per cent. above the standard toxicity pass, and 11 per cent. of those 30 per cent. above.

The sensitiveness of the stock of mice is tested from time to time by means of the standard, so that comparable results may be obtained by workers in different laboratories.

D. G. H.

Sandstone Industry (Silicosis) Scheme, 1929.

UNDER the Workmen's Compensation (Silicosis) Act, 1928 (8 & 9, Geo. 5) the proprietors of stone quarries and firms dealing with sandstone or similar material containing more than 50 per cent. of silica (free or combined) must insure against liabilities in connection with silicosis under the Act. The following Statutory Rules and Orders made under the Act deal with the question of silicosis:—No. 12, 1919; No. 41, 1924; No. 79, 1925; No. 975, 1928; No. 171, 1929.

For the purposes of this Scheme "sandstone" includes ganister, gritstone and quartzite rocks, but does not include rotten-stone or natural sand.

Paragraph 2 (3) (11) of the Sandstone Industry (Silicosis) Scheme, 1929, provides that: "Where an employer satisfies the Secretary of State by chemical analysis carried out in accordance with such conditions as may be prescribed that the sandstone got or manipulated at any mine, quarry or other premises does not contain more than 50 per cent. silica (free and combined), the Scheme shall, as from such date as may be specified by the Secretary of State, cease to apply to any processes carried on at such mine, quarry or other premises on or in connection with the said stone, without prejudice, however, to any rights or liabilities which may have previously accrued under this Scheme."

In order to obtain exemption under this paragraph the Secretary of State has directed (May, 1929) that the chemical analysis for the determination of silica (free and combined) in any sandstone shall be carried out in accordance with conditions specified by the Government Chemist, and the result shall be certified either by an analyst appointed by a local authority under the Food and Drugs (Adulteration) Act, 1928, or by an analyst approved by the Secretary of State.

The conditions specified by the Government Chemist were attached to the Home Secretary's notice; with some little modification they are as follows:

SANDSTONE INDUSTRY (SILICOSIS) SCHEME, 1929.*

DETERMINATION OF SILICA IN SANDSTONE AND ROCKS.

The method for the determination of total silica in sandstone and rocks, at present in use is described in the following scheme. While the method applies in the majority of cases, some rocks may behave abnormally, and in these, special precautions are necessary. No general statement can be made applicable to all such cases.

SAMPLING.—A representative sample of the material should be taken by an expert sampler. The size of the sample will depend on the homogeneity and texture of the material.

PREPARATION OF SAMPLE FOR ANALYSIS.—The sample is broken into pieces of such a size that they may easily be inserted into the percussion mortar to be used in the later stages of pulverisation. After it has been thoroughly mixed, this broken material must be "quartered

* S.R. & O. 1929, No. 171. MASTER AND SERVANT. Workmen's Compensation Act, 1925, dated March 18, 1929. H.M. Stationery Office. Price 5d. net.

down" to a bulk of about half a pound, which is then crushed in a steel percussion mortar until the whole of it can pass through the topmost of a battery of six sieves whose mesh is graded from 5 I.M.M.† (topmost sieve) to 100 I.M.M.† (lowest sieve). The fractions retained by each sieve after a thorough shaking are separately mixed, weighed, and such aliquot portions taken from each that there is obtained a final combined sample of all grades, weighing not less than 10 grms. This is again shaken in the battery of sieves, and the coarser portions are crushed in the percussion mortar until the whole of it passes through the 100 sieve. The final powder is thoroughly mixed and transferred to a closed bottle. Gross particles of iron may be removed from this powder by means of a magnet.

DETERMINATION OF SILICA.—One grm. of the finely powdered sample is mixed with 4 grms. of pure anhydrous sodium carbonate in a platinum crucible, the mixture being covered with a further 1 grm. of the sodium carbonate. The crucible and contents are heated over a Teclu or Meker burner, at first gently, the heat being gradually increased to the full and so maintained for 20–30 minutes until the contents are in a state of quiescent fusion. After a final heating for 5 minutes over the blast, the crucible is cooled by quenching in cold water, and the fused cake is removed as far as possible and disintegrated by heating with water and one drop of alcohol in a platinum dish. Fifteen ml. of concentrated hydrochloric acid (sp. gr. 1.15) are then added slowly, the dish being covered, and after effervescence has ceased, the liquid is evaporated to dryness on a water or a steam bath, heating being continued until the bulk of the hydrochloric acid is removed and the deep yellow colour of the iron chloride has changed to a pale yellow. The dry mass is cooled and drenched uniformly with about 5 ml. of concentrated hydrochloric acid, 100 ml. of water added, and, after solution of the soluble salts by heating, the whole is filtered, and the silica washed, first with cold water and finally with hot, until free from chloride. The filtrate is again evaporated to dryness, the mass is treated with hydrochloric acid and water as in the first evaporation, and the small amount of silica is filtered off, and washed on a separate filter paper. The combined filter papers, and silica, etc., are dried, burned and finally ignited over the blast in a weighed platinum crucible until the weight is constant (A). A few drops of water, 5 drops of sulphuric acid (1:1), and 10 ml. of pure hydrofluoric acid are added to the crucible, and the silica volatilised by evaporation to dryness on a hot plate. The crucible and residue are ignited and weighed (B); the difference between (A) and (B) gives the weight of silica in the sandstone taken.

It is to be noted that the residue after volatilisation of silicon tetrafluoride may contain sulphates which are difficult to break up on heating. In such a case the residue must be ignited again after mixing with pure solid ammonium carbonate.

A blank experiment must be carried out at the same time, using the same number of filter papers and similar quantities of reagents.

† I.M.M. signifies the scale of sieves adopted by the Institute of Mining and Metallurgy.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Invertase from Honey. P. E. Papadakis. (*J. Biol. Chem.*, 1929, **83**, 561–568.)—It has recently been shown by other investigators that invertase from honey differs from invertase from yeast in several ways. Honey invertase shows a characteristic difference from yeast invertase in the beginning of the hydrolysis of sucrose, being activated by β -glucose, whilst yeast invertase is not; and invertase preparations from honey do not hydrolyse raffinose, whereas invertase preparations from yeast do hydrolyse it. An investigation has now been made in order to obtain additional information concerning honey invertase and its properties. Since β -glucose activates honey invertase, the effect of other aldoses, such as

pentoses, on the rate of sucrose hydrolysis by honey invertase was studied. Experiments were also carried out on the retarding influence of mercuric chloride and α -methylglucoside on sucrose hydrolysis by honey invertase, and on the effect of β -glucose on sucrose hydrolysis by honey invertase in the presence of these retardants. The results seem to indicate that, in the case of honey invertase, sucrose hydrolysis is not activated by the pentoses, mutarotated xylose, *d*-arabinose and *l*-arabinose. Mercuric chloride does not retard the rate of sucrose hydrolysis much at P_H 5.7, but the retardation is more pronounced as the P_H decreases from 5.7 to 4.23. The influence of β -glucose is independent of the presence of mercuric chloride. In the presence of α -methylglucoside β -glucose accelerates the sucrose hydrolysis by honey invertase, and when the P_H is varied from 5.84 to 4.2 α -methyl glucoside does not cause much retardation, and does not change the characteristic sucrose hydrolysis curve.

P. H. P.

Melecitose in Linden Dew Honey. F. E. Nottbohm and F. Lucius. (*Z. Unters. Lebensm.*, 1929, **57**, 549-558.)—This substance, which has hitherto only been observed in manna and in dew honey (*cf.* Hudson and Sherwood, *ANALYST*, 1920, **45**, 136), was separated from the sediment deposited in the latter by extraction of the water-soluble portion. The residue was dissolved in hot water, the dextrin precipitated with alcohol, and the filtered solution evaporated and allowed to crystallise. Melecitose is a trisaccharide, probably $3C_6H_{12}O_6-3H_2O$ (mol. wt. 481), with m.pt. 153 to 156° C., and it crystallises in non-hygroscopic masses of white plates or rhombic prisms. It has a slightly sweet taste, is sparingly soluble in water, alcohol and organic solvents, is oxidised by nitric acid to oxalic acid, and reduces Fehling's solution only to a very slight extent. It has a specific rotation of 89.5° (no muta-rotation), but on hydrolysis by 1 per cent. sulphuric acid for 1 hour at 70° C. this falls to 66.2°, on account of the formation of dextrose and turanose, $C_{12}H_{22}O_{11}$ (m.pt. 157° C.; osazone, m.pt. 216° C., with decomposition). On further hydrolysis turanose decomposes into dextrose and laevulose. Melecitose resists the action of fermentation enzymes or *B. coli*, and probably plays an important part in the metabolism of digestion.

J. G.

Formol Titration in the Investigation of Honey. A. Gottfried. (*Z. Unters. Lebensm.*, 1929, **57**, 558-560.)—The method of Tillmans and Kiesgen (*ANALYST*, 1927, **52**, 417) has been tested on a large number of samples of honey, and the formol titration value (c.c. of 0.1 *N* sodium hydroxide solution for 20 grms. of honey in 100 c.c. of water) has been shown to vary from 0.3 to 1.1 for honeys which, according to the tests of Fiehe and of Ley, are suspect, and from 0.6 to 4.0 for genuine honeys. Lund's tannin precipitation figure increases with the formol titration value up to about the formol value 1.3, above which the correspondence is poor.

J. G.

Some Organic Acids of Sugar Cane Molasses. E. K. Nelson. (*J. Amer. Chem. Soc.*, 1929, **51**, 2808-2810.)—The acids of molasses have been determined and found to be formic acid, about 0.1 per cent., and acetic acid, 0.2 per cent.

(volatile acids); aconitic acid, 0.8 per cent.; lactic acid, 0.05 per cent.; and small quantities of malic and citric acids (non-volatile acids). The volatile acids were distilled from 3 kilos. of molasses to which sufficient hydrochloric acid had been added to liberate the combined acids. The distillate was neutralised with standard barium hydroxide solution and evaporated to dryness. The dried salts were weighed, and from this weight and the amount of barium necessary to neutralise the distillate, the proportion of barium formate and barium acetate was calculated. The ester distillation method was used for the determination of the non-volatile acids. They were first precipitated as lead salts from 2 kilos. of molasses. The acids recovered from the lead salts were dissolved in water and extracted 4 times with ether; the ether removed 4.06 grms. of crystalline aconitic acid (m.pt. 185–186° C.). The aqueous solution was then evaporated to dryness, esterified, and the esters (7.8 grms.) fractionated at 10 mm. Less than 1 c.c. distilled under 150° C.; this fraction afforded a hydrazide (m.pt. 178–179° C.), identified as malic hydrazide. Fraction 2 boiled at 160° C. This fraction was saponified, acidified, and extracted with ether, and yielded pure aconitic acid (3 grms.). The third fraction, boiling above 160° C., measured 0.5 c.c. With hydrazine hydrate it formed citric hydrazide (m.pt. 100–103° C.). A direct, continuous ether extraction was made on the acids recovered by precipitation of 3 kilos. of molasses with lead acetate, in order to avoid losses by esterification, and 23.9 grms. of aconitic acid were obtained. The acid solution remaining was neutralised with calcium carbonate, filtered, boiled, and the precipitate deposited was filtered off and dried. This calcium salt, (1.76 grms.) yielded citric acid (m.pt. 142–144° C.). Four hundred grms. of Dominican molasses were acidified, diluted with 200 c.c. of water, and extracted with a rapid stream of ether for 24 hours. The ether-soluble acids were neutralised with barium hydroxide, diluted to 100 c.c., and 200 c.c. of alcohol were added. After standing over-night the solution was filtered, treated with sulphuric acid to deposit barium sulphate, filtered, boiled with an excess of zinc carbonate, and filtered again. The filtrate was concentrated to 5 c.c., 15 c.c. of alcohol were added, and the crystalline precipitate was filtered off, dried, and weighed (0.315 gm.), and proved to be zinc lactate. All the fractions from fractional crystallisation of the acids recovered from the insoluble barium salt were found to be aconitic acid. The establishment of the presence of formic, acetic, aconitic, malic and lactic acids in sugar cane molasses confirms the results of previous investigators. The presence in sugar cane molasses of citric acid has not previously been reported.

P. H. P.

Tests for Methanol. H. Leffmann and C. C. Pines. (*Am. J. Pharm.*, 1929, 101, 584–586.)—Matthes' modification of the German process for the detection of methanol (*Pharm. Ztg.*, 1926, 96), whereby potassium guaiacosulphonic acid is substituted for guaiacol dissolved in strong sulphuric acid, is regarded very favourably. The U.S.P. (X) method is satisfactory, but glycerol (which is not infrequently present in factitious liquors) will simulate the methanol reaction, and, on distillation, glycerol, or some decomposition product thereof, will give a reaction with the magenta and sulphurous acid test; guaiacosulphonic acid, however, will not.

D. G. H.

Use of Ultra-violet Light in the Detection of Refined Oil in Virgin Olive Oil. S. Musher and C. E. Willoughby. (*Oil and Fat Ind.*, 1929, 6, 15-16.)—The fluorescence under the ultra-violet lamp (light reflected from the sample) of virgin olive oils varies from canary yellow to deep orange, that of second-pressing oils being darker, but all refined oils give a characteristic bluish-violet fluorescence. The ultra-violet lamp, used in conjunction with a spectro-photometer, can detect down to 5 per cent. of refined oil in virgin olive oil; without the aid of the spectro-photometer 65 per cent. of refined oil could not be detected. The differences of fluorescence are regarded as due to the varying amounts of chlorophyll present. Californian virgin oils more nearly resemble second-pressing oils from Europe, the reason suggested being the greater proportion of oil extracted from the fruit in the process, and the consequent difference in chlorophyll content. Heating a virgin oil for 30 minutes at 300° C. caused it to fluoresce like a mixture containing 5-10 per cent. of refined oil.

D. G. H.

Water in Strychnine Sulphate. W. Schnellbach. (*Amer. J. Pharm.*, 1929, 101, 587-590.)—Crystallised strychnine sulphate may be either the pentahydrate (monoclinic crystals) formed when crystallisation occurs above 40° C., and containing theoretically 10.51 per cent. of water, or the hexahydrate (tetragonal crystals) when crystallised below 40° C., and having 12.36 per cent. water, and preparations with water contents deviating from the theoretical values of these two forms are considered to be mixtures of the two hydrates.

D. G. H.

Determination of Sparteine. J. Hirt. (*J. Pharm. Chim.*, 1929, 121, 111-115.)—The gravimetric silicotungstic method of Bertrand (1899) is regarded as the most satisfactory for the determination of sparteine. Sparteine silicotungstate is somewhat soluble in water, and the optimum conditions for precipitation are in the presence of 1 per cent. acidity as sulphuric acid. The silicotungstic reagent itself has no influence on solubility.

D. G. H.

Colorimetric Determination of Strophanthins. A. Leullier and H. Griffon. (*Bull. Soc. Pharm.*, 1929, 36, 408-414; *Ann. Chim. anal.*, 1929, 11, 260-261.)—Liebermann's reaction is applied by treating a trace of the glucoside with 2 c.c. of acetic anhydride, followed by 2 c.c. of chloroform, and finally by 2 drops of concentrated sulphuric acid. The olive-green colour is at its maximum in 30 minutes, and the colour is given by all amorphous commercial strophanthins, but ouabain gives a yellow-orange colour. The reaction has also been studied quantitatively. As a modification of Pettenkofer's reaction, a trace of the glucoside is dissolved in 0.5 c.c. of absolute alcohol, 0.1 c.c. of 1 per cent. furfural solution in 95 per cent. alcohol is added, and 0.5 c.c. of concentrated sulphuric acid run in to the bottom of the tube. A blue ring is formed with amorphous glucosides at the point of separation, and a violet-grey ring with the crystallised glucosides.

D. G. H.

Biochemical.

Therapeutic Value of Irradiated Milk in the Treatment of Rickets.

C. Watson, T. Y. Finlay and J. B. King. (*Lancet*, Oct. 5, 1929, 704-707.)—A series of observations has amply confirmed the claims of numerous German writers concerning the value of irradiated milk in the prevention and cure of rickets. For the work the Scholl and Scheidt methods of irradiation were tried, and milk was successfully irradiated by both these processes. The latter is known as "the cold process." Twelve cases of pronounced rickets were selected for treatment, four of which had been under skilled hospital treatment for periods ranging from 3 to 5 months, and had proved unusually refractory to treatment. All medicinal and other special antirachitic measures in use were stopped, the same diet being continued, with the exception that 6 oz. daily of irradiated milk replaced 6 oz. of the 18 oz. of non-irradiated high-grade milk in previous use. The other 8 cases were each given 18 oz. of irradiated milk daily and 18 oz. of non-irradiated milk. Frequent radiological examinations were made at short intervals; attention was directed mainly to the condition of the wrists, knees and ankles. Rapid improvement took place; within 14 days of starting to give irradiated milk it was clear that a remarkable curative influence was at work. In cases of moderate severity radiological evidence of cure was obtained within 4 to 6 weeks, and in extreme cases within 6 to 8 weeks. A strange feature of one very severe case was the coincident improvement which occurred in the mental development of the child; this did not develop noticeably until after 3 weeks' treatment. The authors believe that there could be no justification for the price of irradiated milk exceeding that of non-irradiated milk by more than 1d. per pint. Irradiated milk should be used with care and discrimination. In this country irradiated milk can only be sold under license from the patent holders. Under this arrangement the licensees agree that "their irradiated milk shall not contain less than two (2) ostelin (vitamin D) units per gramme of butter-fat as determined by the P_H drop test under conditions laid down in the papers by Jephcott and Bacharach (*Biochem. J.*, 1926, xx, 1351; 1928, xxii, 60), or, alternatively, eight (8) Pharmaceutical Society's units per gramme of butter-fat as adopted in test by the Pharmaceutical Society." With fuller knowledge, time may show that these tests may require modification. We have at present no assurance that the butter-fat supplies a complete and reliable guide. However, under the existing standards, milk definitely can be successfully irradiated so as to have imparted to it a very valuable additional therapeutic property in the prophylaxis and cure of rickets. Irradiated milk should not be regarded as a complete substitute for good fresh untreated milk. In rickets, between 2 and 5 years of age, excellent results have followed its use when the milk has been used in strengths varying from 1 part irradiated to 2 parts non-irradiated, up to equal parts of the two preparations. The cure of the disease is established more quickly, effectively, and economically by the use of irradiated milk than by various irradiated commercial preparations. There are indications that irradiated milk may prove of outstanding

value in the treatment of certain disorders other than rickets, notably disorders incidental to pregnancy and lactation, the climacteric, malnutrition, injuries and surgical diseases of bone, and certain forms of tuberculosis. The authors consider that there is need for the establishment in this country of a scientific body to initiate and direct the work, both on its strictly scientific and clinical sides, called for by these new facts about nutrition and the influence of ultra-violet rays upon it.

P. H. P.

Heat and Ultra-Violet Irradiation as Means of Differentiating Vitamins B and G in Yeast. C. Kennedy and L. S. Palmer. (*J. Biol. Chem.*, 1929, **83**, 493-496.)—Vitamin *B*, the antineuritic factor, and vitamin *G*, the antipellagric factor, are both necessary for growth; an accurate practical method for the isolation of each factor is, therefore, highly desirable. Hogan and Hunter (*J. Biol. Chem.*, 1928, **78**, 433; *ANALYST*, 1928, **53**, 505) proposed what seemed to be a promising method for destroying the antipellagric vitamin and leaving intact the antineuritic vitamin in yeast. They found that yeast, irradiated under certain conditions, loses its so-called growth-promoting properties, and retains its antineuritic activity, and that autoclaved yeast, which possesses no antineuritic potency, corrects the deficiency of the irradiated yeast. The authors, in continuing their investigations on yeast (*J. Biol. Chem.*, 1928, **76**, 591) as a source of the growth-promoting factors, have not been able to substantiate these results of Hogan and Hunter. Irradiated yeast, as a source of the growth-promoting factors, vitamins *B* and *G*, has been tested both alone and in conjunction with autoclaved yeast. A figure gives the composite growth curves obtained with the feeding trials. The control group of rats, Lot 1, received daily 0.5 gm. of untreated dry starch-free yeast to supply vitamins *B* and *G*, those of Lot 2 autoclaved yeast, those of Lot 3 irradiated yeast, and those of Lot 4, 0.5 gm. of a mixture of equal parts by weight of autoclaved and irradiated yeast. The rate of growth of the rats in Lot 3, as shown by the graphs, was very good; thus irradiation could not have completely destroyed the antipellagric factor. The rate of growth of the rats in Lot 4 did not quite equal that of the rats in Lot 1. It is very probable, therefore, that irradiation and autoclaving impair in varying degrees both vitamin *B* and vitamin *G*. Two further groups of rats were given a ration that differed from the others in that it contained, in addition, the alcoholic extract of 15 grms. of ether-extracted wheat embryo; this ration was thought to contain ample quantities of vitamins *B* and *G*, but it failed to promote growth, and became growth-promoting when small quantities of autoclaved yeast were added. The curves of Lot 5 show that this ration also became growth-promoting when supplemented with the irradiated yeast; an additional supplement of autoclaved yeast (Lot 6) did not enhance the rate of growth over that of the irradiated yeast alone. Therefore, irradiation cannot be relied upon completely to destroy the growth-promoting factors of yeast other than the antineuritic factor.

P. H. P.

Quantitative Studies of Responses to Different Intakes of Vitamin D. H. C. Sherman and H. K. Stiebeling. (*J. Biol. Chem.*, 1929, **83**, 497-504.)—A quantitative study has been made of the effect of graded allowances of vitamin *D*

upon growth and calcification in young rats receiving a basal diet adequate in other respects, but decidedly deficient in vitamin *D*. The diet used consisted of extracted casein, 18 per cent.; Osborne and Mendel salt mixture, 4 per cent.; dry brewers' yeast, 10 per cent.; sodium chloride, 1 per cent.; dried spinach, 1 per cent.; and corn-starch, 66 per cent. The results show that in young rats reared by mothers on a diet consisting largely of two-thirds ground whole wheat, and one-third whole milk powder, and transferred at the 21st or 28th day of age to the vitamin-*D*-deficient diet, practically normal calcification resulted by the 56th day of age in cases in which the basal diet had been supplemented by somewhat more than 5 per cent. of the calories from whole (summer) milk powder, and by the 80th day of age in cases in which the basal diet had been supplemented during the preceding 4 weeks by the same milk powder to the extent of 8 to 9 per cent. of the calories. Smaller graded portions of milk produced corresponding improvements in calcification over their respective negative controls. The experiments reported afford extensive and convincing evidence in confirmation of the fact that cow's milk as ordinarily produced in the U.S.A. contains important amounts of vitamin *D*. The deposition of calcium in the femurs appears to be more closely proportional to the supplementary vitamin *D* furnished than does gain in weight. The improvement in growth, due to additional vitamin-*D*-containing material between the 21st and 56th days, is too small for the growth during that period to be used as a quantitative measure of the vitamin *D* furnished; however, a figure shows that after giving the vitamin *D*-deficient diet for a month, grading the allowance of vitamin *D* is then reflected by the gain in weight. There is additional evidence that the test animals had considerable bodily stores of vitamin *D* which must have come from the milk consumed by themselves and their mothers. Equally consistent responses in calcification were obtained under the conditions of these experiments when the experimental period followed immediately upon separation of the young from their mothers as when it was preceded by prolonged feeding of the vitamin *D*-deficient diet. This procedure insures vigorous animals, and permits the 4- or 5-week experimental period to be terminated at an early age, thus making use of the period of most rapid deposition of calcium, as well as reducing the time and expense involved in experimental work. The percentage of calcium in the fresh femur is proportional to the supplementary vitamin *D* furnished within a sufficient range of values to permit of reasonably quantitative comparisons, when sufficient numbers of well-controlled experiments are performed. P. H. P.

Toxicological.

New Derivatives of *p*-Phenylenediamine and their Value as Hair-Dyes. H. Meyer. (*Chem. Ztg.*, 1929, 53, 765-766.)—Para-phenylenediamine, formerly used for dyeing hair, has an irritant action on the skin, whereas the less markedly basic *p*-toluylenediamine, *p*-aminodiphenylamine and phenylenediamino-sulphonic acids cause little, if any, such action. Moreover, since those whose heads perspire intensely are particularly prone to hair-dye dermatitis, this trouble

is probably due to the formation of salts of the diamine with the perspiration acids. Under conditions similar to those prevailing on the head, *p*-phenylenediamine, *p*-toluylenediamine, and *p*-aminodiphenylamine all form salts with butyric acid, but this salt-formation proceeds readily and considerably only with the first of these bases. Various compounds of these bases with carboxylic acids, such as salicylic, gallic and benzoic, when mixed with hydrogen peroxide solution, exhibit satisfactory hair-dyeing properties, and result in no harmful effects.

T. H. P.

Methyl Chloride Poisoning. Kegel, McNally and Pope. (*J. Amer. Med. Assoc.*, Aug. 3, 1929, 353; *Brit. Med. J.*, Oct. 5, 1929, 633.)—Methyl chloride is used to a very large extent in domestic refrigerators in America, and has been found to be the cause of much illness and many deaths. It is odourless, and, therefore, all the more dangerous. It is decomposed in the human body into methyl alcohol, which destroys nervous tissue and causes degenerative changes in the heart, liver and kidneys. The symptoms are drowsiness, and nausea with vomiting. Blood appears anæmic, and the urine may contain formic acid, diacetic acid and acetone. Halogen derivatives of aliphatic hydrocarbons appear to be more toxic than the hydrocarbons themselves, not by the action of the halogen alone, but of the whole molecule.

R. F. I.

Agricultural.

Determination of Ammonia in Soil and the Adsorption Power of Soil for Ammonia. C. Olsen. (*Compt. rend. Lab. Carlsberg*, 1929, 17, No. 15, 1–20.)—The determination of ammonia in soils by direct distillation with alkali is suspect on account of the liberation of the ammonia from nitrogen in the organic matter present, while extraction by water is incomplete under ordinary conditions, owing to adsorption of ammonia by the soil. It is, therefore, proposed that 100 grms. of fresh broken soil (or 50 grms. of peat) should be shaken in a bottle for 1 hour with a few drops of toluene, 200 c.c. of *N* potassium chloride solution and sufficient hydrochloric acid (determined by trial with Congo red paper) to bring the P_H of the suspension to 1.0 ± 0.3 . The P_H of the filtered extract is determined by means of methyl violet, and the correction $+0.45$ applied for the salt error of potassium chloride. Ammonia is determined by distillation of 100 c.c. with 200 c.c. of water and 4 grms. of magnesia into an excess of standard sulphuric acid, which is then boiled and back-titrated. Allowance must also be made for the blank on the reagents and for the water-content of the soil. If the contents of the distillation flask are then again diluted to 300 c.c. and 3 grms. of Devarda alloy added, the nitrate nitrogen may be determined on the same portion of the filtrate. Comparative extractions with water and with the above salt solution of 2 peat, 2 clay and 2 sandy soils (P_H values 3.7 to 7.6) showed that the adsorption capacities for ammonia decreased in the order mentioned, irrespectively of the P_H value, and that most ammonia is adsorbed when the total ammonia content of the soil is highest.

J. G.

Organic Analysis.

Chia Seed Oil. W. F. Baughman and G. S. Jamieson. (*Oil and Fat Ind.*, 1926, 6, 15-17.)—Oil from the seed of the Mexican chia plant (*Salvia hispanica*, L.) had the following characteristics:—Sp. gr. $25^{\circ}/25^{\circ}$, 0.9358; n_D^{20} , 1.4838; saponification value, 194.8; iodine value (Hanus), 190.0; thiocyanogen-iodine value, 113.2; unsaponifiable matter, 0.7 per cent.; acid value, 1.4; loss of weight on heating 3 hours at 110° in carbon dioxide, 0.3 per cent.; hexabromide number of fatty acids, 51.2; saturated acids (corrected), 8.1; unsaturated acids (corrected), 85.2 per cent., of iodine value 214.6. The composition of the unsaturated acids in the original oil was: linolenic, 39.3; linolic, 45.2; and oleic acid, 0.7; and of the saturated acids: myristic, 0.14; palmitic, 4.90; stearic, 2.73; and arachidic, 0.33 per cent.

D. G. H.

Malayan Lumbang Oil. T. H. Barry. (*J. Soc. Chem. Ind.*, 1929, 48, 239T-290T.)—A sample of lumbang oil from nuts grown on the Government experimental station at Serdang in the Malay States had the following characteristics:—Sp. gr., 0.9264; n_D^{20} , 1.4764; saponification value, 192.1; iodine value, 150.8; unsaponifiable matter, 0.41 per cent.; acid value, 0.66; and coefficient of expansion at $12.5-46^{\circ}$ C., 0.00063. The iodine value is lower than that recorded for Phillippine oil. It was possible to detect with certainty lumbang oil added to China wood oil by using the Brown heat test; but the maximum limit of 12 minutes is not exceeded until 20 per cent. is present. Lumbang oil alone is not suitable as a paint medium in this country, although it might be in a drier and warmer climate. The drying time under laboratory conditions was double that of linseed oil. D. G. H.

Separation of Cystine from Histidine. H. B. Vickery and C. S. Leavenworth. (*J. Biol. Chem.*, 1929, 83, 523-534.)—In acid solution cystine forms a silver compound which becomes increasingly insoluble as the acidity of the solution is reduced. At P_H 6.0 nearly all the cystine present in such a solution is precipitated. Data are given which show that this amino acid is precipitated more or less completely by every heavy metal reagent that is customarily used to throw down histidine; it is, therefore, probable that cystine has been present as an impurity in the final histidine fractions secured in most protein analyses. The copper compound of cystine is very insoluble, and separates readily and completely when a solution of cystine is boiled with an excess of copper hydroxide and cooled. Under the same circumstances histidine remains in solution. Therefore to separate these two amino acids the solution containing them is boiled for 30 minutes with excess of copper hydroxide, allowed to stand at least 30 minutes, and then filtered to remove the cystine copper and excess copper hydroxide. Copper is subsequently removed from the filtrate by hydrogen sulphide, and the solution is treated in the usual way for the determination of histidine as dinitronaphtholsulphonate. Histidine fractions can be determined with greater ease and accuracy by this procedure. The precipitation of cystine by copper hydroxide was investigated both with preparations of pure plate cystine ($[\alpha]_D^{20} = -215^{\circ}$) and partially racemised

"needle cystine" ($[\alpha]_D^{20} = -41^\circ$), and both compounds were almost completely precipitated. Colorimetric determinations for cystine were carried out on the filtrates after removal of the copper. As an illustration of the application of this procedure, an analysis of the basic amino acids of human hair has been carried out, which indicates that this tissue yields 0.5 per cent. of histidine, 8.0 per cent. of arginine, and 2.5 per cent. of lysine. A colorimetric determination of cystine on the same sample indicated that 16.5 per cent. of cystine was present. P. H. P.

Inorganic Analysis.

Use of Phenolic Acids in the Detection, Separation and Determination of Metals. Part I. Separation of Group 2A Metals. P. N. Das-Gupta. (*J. Indian Chem. Soc.*, 1929, 6, 627-633.)—(a) The precipitated sulphides of mercury, bismuth, lead, copper and cadmium are digested with 6 *N* nitric acid, the residue tested for mercury, and the filtrate boiled to remove hydrogen sulphide, neutralised with sodium hydroxide till a permanent turbidity appears, again boiled, and a slight excess of a fresh 1 per cent. gallic acid solution added. Bismuth may then be filtered off as a light yellow crystalline precipitate, and the filtrate (diluted if much bismuth or cadmium is present) boiled with a slight excess of sodium acetate solution to precipitate lead and copper, whilst the cadmium remaining in solution is precipitated as sulphide. Lead and copper are separated by the action of hydrogen peroxide and an excess of ammonia, which dissolve the latter in hot solutions. (b) If the metals are in nitric acid solution, sodium hydroxide is used to render the reaction faintly acid, an excess of a fresh solution of β -resorcylic acid added, and the mixture boiled and well stirred. Mercury gives a white or yellow precipitate, soluble in acid, and the filtrate may be treated as before. The optimum conditions for the reaction of these phenolic acids, with the metals concerned, have been examined in detail. J. G.

Volumetric Method for Determining Silver in Presence of Halides and Cyanides. H. Baines. (*J. Chem. Soc.*, 1929, 2037-2041.)—None of the known methods is applicable directly to the routine determination of silver occurring as halides in photographic products containing cyanides and small unknown and variable amounts of other substances which react with cyanide. If the silver is dissolved in a slight unknown excess of potassium cyanide solution and standard iodine is run in until one drop produces a faint permanent opalescence, the excess of potassium cyanide has then completely reacted with the iodine, $\text{KCN} + \text{I}_2 = \text{KI} + \text{CNI}$. If now starch is added and the titration with iodine continued until a permanent blue colour appears, the silver complex has reacted completely with the iodine, $\text{KAg}(\text{CN})_2 + 2\text{I}_2 = \text{KI} + \text{AgI} + 2\text{CNI}$. Thus, the volume of iodine added between the two stages determines the silver, and the total iodine added the cyanide. The opalescence is better defined if an electrolyte is present.

A quantity of material containing 0.05 to 0.09 grm. of silver is dissolved in 5 to 9 c.c. of approximately 0.2 *N* potassium cyanide solution containing 5 c.c. of

ammonia (0.880) per litre, 50 c.c. of 10 per cent. sodium chloride solution being added, and 0.1 *N* iodine solution run in from a burette until a faint opalescence persists; if this point is over-run, it may be re-adjusted after addition of a little cyanide solution—in known quantity if cyanide is to be determined. The liquid is now diluted to 900–1000 c.c. (or correspondingly more if more cyanide than the quantity given were added) with tap water, and 5 c.c. of 0.5 per cent. starch solution are added, the titration being continued till a permanent blue colour appears. The method gives consistent and accurate results. T. H. P.

Separation of Lead and Bismuth. H. Blumenthal. (*Z. anal. Chem.*, 1929, 78, 206–213.)—The sample (10 grms.) is dissolved in dilute nitric acid (16 c.c. of acid, sp. gr. 1.4 and 60 c.c. of water), cooled, diluted to 150 c.c. and a 10 per cent. solution of sodium carbonate added, till all the lead carbonate is precipitated. It is then re-dissolved by addition of sufficient acid to render the solution acid to methyl orange, and the carbon dioxide boiled out. A paste of mercuric oxide is then freshly prepared from pure sodium hydroxide and 5 per cent. mercuric chloride solutions, washed free from alkali by decantation with water, and a slight excess added to the solution with 100 c.c. of cold water. After 12 hours the precipitate, which contains basic bismuth nitrate, is filtered off, the filtrate re-treated with mercuric oxide if it is still turbid, and the precipitate washed with 0.1 per cent. potassium nitrate solution till the washings give no lead sulphate precipitate with sulphuric acid. It is then dissolved in nitric acid, and the bismuth determined colorimetrically by the iodide method. If bismuth is present in relatively large quantities, the final acid solution (100 c.c.) is boiled, and 20 c.c. of a 5 per cent. solution of ammonium phosphate added, a drop at a time, and the bismuth phosphate filtered from the cool solution and weighed. The bismuth was recovered completely from mixtures of 8 grms. of lead nitrate with 0.3 to 50 mgrms. of bismuth, and from mixtures containing 50 per cent. of each metal. Slight modifications are necessary in the presence of arsenic, antimony and tin, and methods of removal of these metals are described. J. G.

Application of the Thiocyanate Method for the Precipitation of Copper in the Confirmatory Tests for Cadmium and Antimony. A. F. Daggett. (*J. Amer. Chem. Soc.*, 1929, 51, 2758–2759.)—The insolubility of cuprous thiocyanate in dilute sulphuric and hydrochloric acids and the ease of precipitation make the thiocyanate method well suited for application to the qualitative scheme of analysis. The means for the separation of copper from cadmium in the confirmatory test for cadmium given by Noyes, "*Qualitative Chemical Analysis*" (1928, 80), has not been found satisfactory for demonstration purposes, but the following thiocyanate method has given very satisfactory results: To the part of the ammonium hydroxide solution, which remains after the ferrocyanide test has been made for the confirmation of copper, dilute sulphuric acid is added until the solution is acid to litmus, and then 5 c.c. of *N* potassium thiocyanate solution; a brown coloration results, due to the formation of cupric thiocyanate. The solution is heated to boiling, about 0.5 gm. of dry sodium sulphite is added, and boiling

continued for about 1 minute, until the white precipitate of cuprous thiocyanate has coagulated. The precipitate is then filtered off, and the clear filtrate is saturated with hydrogen sulphide, when the characteristic yellow precipitate of cadmium sulphide forms if cadmium is present. To avoid the interference of copper in the test for antimony, as given by Noyes, this procedure may be used to advantage after the antimony and tin have been separated from the arsenic by concentrated hydrochloric acid, and the solution has been diluted to the proper acid concentration for the precipitation of the antimony sulphide. P. H. P.

Volumetric Determination of Tin. H. Wolf and R. Hellingötter. (*Chem. Ztg.*, 1929, 53, 683.)—For tin-antimony alloys 0.1 to 0.4 grm. is warmed with a mixture of 50 c.c. of hydrochloric acid (sp. gr. 1.19) and 10 c.c. of a solution of ferric chloride (100 grms. in 50 c.c. of HCl of sp. gr. 1.12), and the tin then completely reduced to the stannous state by the action of 3 iron nails, 8 cm. long, in the presence of 50 c.c. of water and in an atmosphere of carbon dioxide on the water bath for 8 minutes (for 0.1 grm. of tin). The cool solution is filtered on a folded paper sprinkled with *ferrum redactum*, the paper washed, and the filtrate titrated with 0.1 *N* iodine solution with a starch indicator. For copper-tin alloys 1 to 3 grms. of metal are dissolved in 10 c.c. of concentrated nitric acid, the diluted solution filtered, and the residue washed with hot water, dried, mixed with sodium peroxide, and strongly ignited in an iron crucible. The residue is extracted with water, and sufficient hydrochloric acid (sp. gr. 1.19) added to dissolve the iron hydroxide and produce a 50 per cent. acid solution, and reduction carried out as above. Lead-tin alloys (3 to 5 grms.) are digested with 50 c.c. of hydrochloric acid, and the residue treated with potassium chlorate in the presence of a little more acid. The total soluble portion is made up to 500 c.c. in 50 per cent. acid, filtered, and reduced as before. J. G.

Study of the Use of Aurintricarboxylic Acid for the Colorimetric Determination of Aluminium. O. B. Winter, W. E. Thrun and O. D. Bird. (*J. Amer. Chem. Soc.*, 1929, 51, 2721–2731.)—The spectrographic method for the determination of small amounts of aluminium has an advantage over colorimetric methods in that it requires no chemical reagents, for aluminium contaminates nearly all reagents; but the apparatus is very expensive. Of the colorimetric methods which have been proposed, the most promising is the one making use of the ammonium salt of aurintricarboxylic acid, the dye commercially known as aluminon. Attempts to determine the aluminium in plants by modifications of this method used by various investigators did not give satisfactory results. A further study was, therefore, made of the reaction between aluminium and the dye, and the method has now been modified so that samples ranging from 0.0050 to 0.0700 mgrm. of aluminium may be compared with one standard, and the amount of aluminium in each sample may be read directly from a curve. The results are accurate to within about 5 per cent. Special emphasis was placed on the determination of suitable conditions (1) for the formation of a lake of maximum colour intensity, and (2) for destroying the colour of the excess dye while retaining the

lake colour. Maximum colour intensity was obtained in the presence of 10 per cent. of 6 *N* ammonium acetate when the solution was at approximately P_H 4.0, and kept at a minimum temperature of 80° C. for about 10 minutes. In the presence of 5 c.c. each of 5 *N* ammonium acetate and ammonium chloride the dye changed colour at about P_H 7.0. A neutral or alkaline solution of 2 c.c. of 0.1 per cent. dye in a volume of 50 c.c. was very nearly colourless. The lake colour remained sufficiently permanent for determinations to be made until the solution was raised to P_H 7.4. The presence of ammonium acetate and chloride as buffers was found advantageous for controlling the P_H of the solution. Ammonium carbonate was found to be more suitable for the decolorisation of the excess dye than either ammonium hydroxide or a solution of ammonium carbonate in ammonium hydroxide. The procedure for aluminium determinations is as follows:—The solutions, which should be slightly acid, are transferred to 50 c.c. volumetric flasks, and each made up with water to about 20 c.c.; then 5 c.c. of 5 *N* ammonium acetate, 5 c.c. of 1.5 *N* hydrochloric acid and 2 c.c. of 0.1 per cent. dye are added, and the flasks are placed in a water-bath at about 80° C. for 10 minutes. Five c.c. of 5 *N* ammonium chloride are then added, the flasks cooled to room temperature, 5 c.c. of 3.2 *N* ammonium carbonate added, with gentle shaking, distilled water added to the mark, and the contents of each flask mixed. The reactions should then be P_H 7.1–7.3, and the red colour of a blank should disappear in about 15 minutes. (The exact concentration of the reagents is not important, but the final P_H is, and the amount of ammonium carbonate necessary to give this P_H should be found by neutralising similar solutions without adding the dye). A standard (or standards) containing a given quantity of aluminium should be treated simultaneously. After standing for 20 minutes for the excess dye to become decolorised, the colour intensities are compared, and the amounts of aluminium are read from a curve plotted as follows:—When a small number of determinations are to be made, four standards containing 0.0100, 0.0300, 0.0500 and 0.0700 mgrm. of aluminium, respectively, are prepared, and these are treated like the samples. All these solutions are compared with the standard containing 0.0300 mgrm. of aluminium, and the results are calculated to a colorimeter reading of 30 for this standard. Arbitrarily 0.0050 mgrm. of aluminium is given a reading of 100, and with this and the 4 readings of the standards a curve is plotted (colorimeter readings against mgrms. of aluminium), from which the quantities of aluminium in the samples are read. For a large number of determinations, over a period of time, several series of standards should be determined, and a curve plotted from the averages; then only one standard need be used each time determinations are made, and results may be read from the same.

P. H. P.

Electro-Analytic Determination of Thallium as Thallous Oxide. A. Jilek and J. Lukas. (*Collect. Trav. Chim. Czechoslovak*, 1929, 1, 417–428.)—The solution containing less than 0.25 grm. of thallium as thallous nitrate is electrolysed in a platinum dish (anode) in the presence of 1 to 2 grms. of 40 per cent. hydrofluoric acid, with a rotating platinum disc as cathode, at 2 to 5 volts and a

current density of 0.2 amp./cm². After 1 hour the thallium is completely deposited, but on both electrodes, and is removed from the cathode by addition of 1 c.c. of 30 per cent. hydrogen peroxide, without interrupting the electrolysis. It is then re-deposited on the anode as the compound $Tl_2O_3 \cdot HF$, which was found by analysis to contain 84.44 per cent. of thallium. Additions of hydrogen peroxide are necessary at the end of every hour till the electrolyte gives no reaction for thalious ions with potassium iodide or sodium sulphide (usually after 4 hours). The deposit is washed with water without interruption of the current, rinsed with alcohol and dried at 110° C. The fall in voltage produced, on addition of the peroxide, is recovered when this has decomposed. High results are obtained in the presence of alkali salts, especially sulphates, which are retained in the anodic deposit, although traces of thallium remain in solution. In such cases thallium should be removed as thalious sulphide, by the action of sodium sulphide on a hot solution of thalious nitrate and sodium carbonate, and re-dissolved in nitric acid.

J. G.

Determination of Strontium and Barium. L. Szebellédy. (*Z. anal. Chem.*, 1929, 78, 198–206.)—A solution containing 0.5 gm. of the mixed nitrates is evaporated with 50 c.c. of sulphate-free hydrobromic acid, the residue dried for 1 hour at 100° C. and extracted with 3 c.c. and 7 c.c. portions of *iso*-butyl alcohol, the mixed bromides being heated with the alcohol in a dish placed in a closed block of lead maintained at 110° C. for 10 minutes (*cf. id.*, 1927, 70, 39). The mixture is then transferred to a suitable filter moistened with the alcohol, and the clear filtrate evaporated in a tared dish, dried at 100 to 110° C., and dissolved in a minimum amount of water, which is then saturated with an excess of ammonium sulphate. The residue, after evaporation, is dried at 100° C. for 30 minutes, and heated, gently at first, and then strongly, for 20 minutes after fuming has ceased, and the cool residue weighed as strontium sulphate. The barium bromide is removed from the filter in 25 c.c. of hot water, the solution concentrated on the water-bath, and sufficient hydrobromic acid added to make a total of 1 gm. It is then washed into a tared covered dish, evaporated, dried at 180° C. for 30 minutes, and re-dried after addition of a drop of butyl alcohol, cooled and weighed.

J. G.

Analysis of Japanese Allanite. Y. Minami. (*Japanese J. Chem.*, 1929, 4, 1–5.)—The sample was powdered in an agate mortar, 1 gm. decomposed by concentrated hydrochloric acid, and the silica rendered insoluble by repeated evaporations and filtered off. Rare earths were removed from a hydrochloric acid solution of the precipitate produced with ammonia in the presence of ammonium chloride by precipitation with oxalic acid, and iron was then precipitated as sulphide in the filtrate in the presence of tartaric acid. After decomposition of organic matter in the new filtrate by means of hot sulphuric and nitric acids, aluminium and titanium were obtained as hydroxides and weighed as oxides, the titanium being determined colorimetrically after fusion of the oxide mixture with potassium bisulphate. The precipitate of rare earth oxalates was ignited, and the resulting oxides converted into nitrates, thorium being separated by addition of hydrogen

peroxide, whilst cerium was precipitated as iodate. The new filtrate was then saturated with potassium sulphate and the yttrium and cerium groups separated. Other metals were determined in the usual way, and the formula $4R''O, 3R'''O_3, 6SiO_2, H_2O$ was derived from the analysis, where R'' is Ca, Mn or Fe, and R''' is Al, Fe, Ce, Y, etc. Analysis of the arc and absorption spectra of each fraction revealed germanium (in the tin fraction), holmium, erbium, thulium, praseodymium, neodymium, dysprosium, lanthanum, samarium, and ytterbium. J. G.

Micro-determination of Selenium and Tellurium in Organic Compounds. H. D. K. Drew and C. R. Porter. (*J. Chem. Soc.*, 1929, 2091–2095.)—In the determination of selenium in organic compounds by converting it into the dioxide by heating with nitric acid in a Carius tube and subsequently precipitating the selenium by means of sodium sulphite, it is found to be unnecessary to remove the nitric acid. Passage of sulphur dioxide into the solution in presence of excess of hydrochloric acid suffices to destroy the nitric acid and to bring about, after an interval, the quantitative precipitation of selenium.

From 5 to 20 mgrms. of the material (3 to 5 mgrms. of selenium) are decomposed in a micro-Carius tube with about 0.3 c.c. of fuming nitric acid (d 1.5). The contents of the tube are washed into a boiling tube with alternate rinsings of water and concentrated hydrochloric acid, and the liquid (about 10 c.c.) is heated on a boiling water-bath while a stream of sulphur dioxide is passed through it. When the whole of the selenium is transformed into the black variety (about 20 mins.), the liquid is cooled and filtered through a Pregl micro-Gooch crucible (provided with a capillary cap to stabilise the humidity condition of the asbestos) with the aid of a siphon tube, the vessel and delivery tube being thoroughly rinsed with water and alcohol. The capped tube is dried at 110° during ten minutes in a stream of filtered air, and weighed with the usual precautions. The contents of the filter need not be changed for a further estimation, even after long standing; but, after 24 hours, the filter should be re-washed with water and alcohol, dried and again weighed before use. Not less than about 2.5 mgrms. of selenium should be weighed.

With a tellurium compound, 10 to 15 mgrms. are decomposed with fuming nitric acid (d 1.5) in a Carius tube (0.3 c.c. of acid) or a micro-Kjeldahl flask (3–4 c.c. of acid), the liquid being then rinsed into a small porcelain dish with water, and evaporated to dryness on a water-bath. The residue is dissolved in 3 c.c. of 10 per cent. hydrochloric acid and the solution evaporated to a syrup. The dish is covered with a small clock-glass, and 10 per cent. hydrochloric acid (3 c.c.) is added, followed by freshly prepared, saturated aqueous sulphurous acid (3 c.c.) and 15 per cent. aqueous hydrazine hydrochloride (2 c.c.). The mixture is heated for ten minutes on a water-bath with gradual addition of more sulphurous acid (2 c.c.), and the tellurium is then filtered off and washed with hot water and alcohol. The crucible is dried and weighed as with selenium. Precipitated selenium and tellurium show no tendency to oxidise.

Chlorine, bromine and iodine may be determined accurately on a micro-scale, even in presence of tellurium. Chlorides and bromides may be decomposed by heating in micro-Kjeldahl flasks with concentrated nitric acid containing excess of silver nitrate, but iodides should be decomposed with aqueous halogen-free potash before the iodine is precipitated, in the cold, with nitric acid containing silver nitrate. Fuming nitric acid should not be used, as it causes minute but appreciable losses of halogen, whether tellurium is present or not. T. H. P.

Physical Methods, Apparatus, etc.

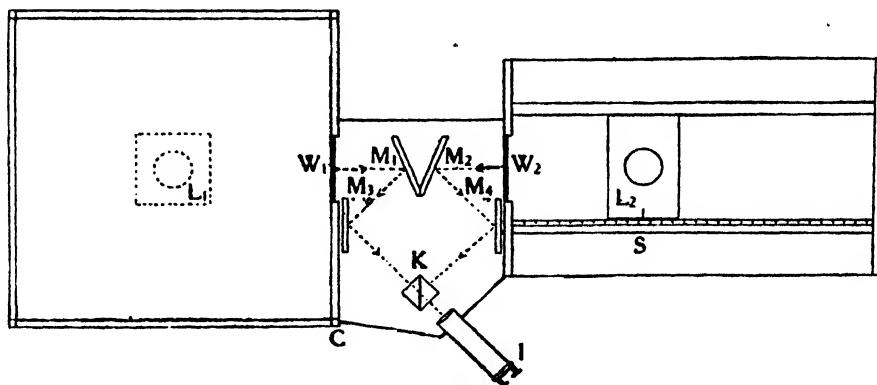
Distinction of Pigments in Ultra-Violet Light. M. J. Schoen and J. Rinse. (*Chem. Weekblad*, 1929, 26, 321-322.)—The examination of a large number of white pigments has shown that great care must be exercised in drawing conclusions from the results, as different samples of the same pigment (e.g. lithopone) may show different colours if they are of different origin. Also, so-called pure zinc whites containing less than 2 per cent. of lead white had the same fluorescence as zinc white of high lead white content. The fluorescence of zinc white may vary between green, brown and light yellow, whilst that of lead white is green-brown, though of less intensity. Natural chalk was distinguishable from precipitated chalk in the authors' samples, as the former appeared dark yellow and the latter black. Aluminium hydroxide showed a fine light-blue colour, and titanium-zinc oxide pigments (with one exception) bright violet, whilst organic dyes (e.g. imitation red lead) were easily recognisable. There is no relation between the fluorescence of lithopone and its fastness to light. J. G.

Cube Photometer for Comparing the Whiteness of Fabrics. A. Adderley. (*J. Text. Inst.*, 1929, 20, T203.)—The photometer described measures not only the total amount of light reflected by a fabric (intensity), but also the distribution of the light reflected by the surface of a fabric at various angles (colour). The latter specifies the lustre or "finish" of the surface. The apparatus consists of a hollow cube ABCD, 14" internal measurement, the interior of which is painted with several coats of a special zinc oxide paint having a reflection factor of 94 per cent., which is greater than that of any fabric yet found. The faces AB, CD, DA are detachable, and may be covered with the material under examination. The face BC is fitted with an opal window W_1 , 2 sq. in. The top of the cube has a central circular hole through which shines a 12-volt gas-filled lamp L_1 , casting a circle of illumination on the floor of the cube, no other part of the interior being directly illuminated. The photometric arrangements consist of a Lummer-Brodhun prism, K, and the mirrors M_1 to M_4 . A second opal window is fitted at W_2 , and is illuminated by the lamp L_2 , similar to, and in series with, L_1 , on a 24-volt accumulator, and moving over a scale S, which indicates the distance from the lamp to W_2 . Lamp L_2 is moved until W_1 is of the same illumination as W_2 , and the reading on scale S is noted. The brightness of W_2 is proportional to $1/d_1^2$

where d is the scale reading, and whence the brightness of W_1 can be calculated.

If one of the painted faces is now covered with fabric and the lamp again adjusted till the windows are equally illuminated, a new brightness figure is obtained $1/d_2^2$. The reflection or intensity factor compared with that of the paint can be written as a function of $(\frac{d_1}{d_2})^2$.

The measure of the intensity is expressed as a percentage of the light which would be reflected from the specially painted surfaces. This measure, however,



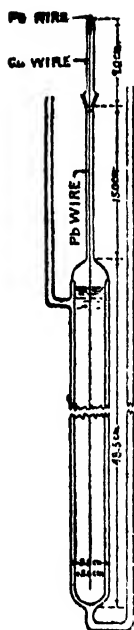
does not describe the manner in which the fabric departs from white. It is conceivable that two fabrics, one on the yellow side and one on the blue side, would give the same intensity.

The colour can be measured with the cube photometer by employing colour filters at position F. The photometer is calibrated by measuring the intensity of light when the face AD is partly covered with squares of paper of known area blacked with carbon black, but with the use of a different colour filter (red, green and blue) for each series and plotting a curve for each showing the value of $(\frac{d_1}{d_2})^2$ against the percentage of total whiteness for each colour.

The article is printed on two kinds of white paper of two tints, of which the per cent. brightness and percentages of excess red and excess blue are given in order to illustrate the measurements described.

R. F. I.

A Laboratory Ozoniser. A. L. Henne. (*J. Amer. Chem. Soc.*, 1929, **51**, 2676–2677.)—An inexpensive apparatus is described which is a simplification of the ozoniser described by L. I. Smith (*J. Amer. Chem. Soc.*, 1925, **47**, 1844). The figure, which shows one of the ozone tubes, is self-explanatory. A lead wire dipping in dilute sulphuric acid is used as one of the electrodes; the lead wire (six fuse-wires twisted together) remains straight and centred by virtue of its own weight, so that sparking is prevented. As in the apparatus of Smith, three tubes



are sealed in series, and almost completely immersed in a bath of water in a battery jar. The water is used as a second electrode and as a cooling medium. No mercury is used, and the weight of the tubes is nearly counterbalanced by the weight of the water displaced; therefore, to maintain the tubes in position a plate of bakelite is blocked 3 cm. from the bottom of the battery jar, and fitted with slots to hold the lower extremities of the tubes, and the lid of the battery jar is fitted with corresponding slots (except that the diameter of the holes is 4 cms. instead of 3.5 cms.). The tension (10,000 v.) between the electrodes is furnished by a $\frac{1}{4}$ -kw. transformer. Complete drying of the oxygen is very important. The yield of ozone is substantially the same as that indicated by Smith; the percentage weight of ozone is about 14 per cent., 8 per cent. and 3 per cent. when oxygen is delivered at the rate of 4, 20 and 100 litres per hour, respectively. This corresponds to an hourly output of 0.7, 3.6 and 4.6 grms. of ozone. With this apparatus the oxidation of double linkages by means of ozone is exceedingly simple.

P. H. P.

References to Scientific Articles not Abstracted.

THE NATURE OF THE COLOUR OF POTTERY, WITH SPECIAL REFERENCE TO THAT OF ANCIENT EGYPT. By A. LUCAS. *J. Roy. Anthropol. Inst.*, 1929, **69**, 113-129.

Red pottery—Gray and drab pottery—White pottery—Black pottery—Red and black pottery—Oxides of iron and their preparation—Deductions as to the preparation and composition of Ancient Egyptian pottery.

SILICA IN MINERAL WATERS. By P. HEFFERMAN. *Arch. Med. Hydrology*, 1929 (May).

Silica in thermal spa waters is mainly a colloidal hydrosol—In this state it cannot be determined in terms of silica or silicon ions—Activities of such spa waters are (a) adsorptive and (b) coagulant—They depend upon the "selectivity" of the colloid.

PHOTOMICROGRAPHS OF PHILIPPINE STARCHES. By R. N. ALLEN.

Forty-five photomicrographs, with descriptions, of starches from different kinds of Philippine tubers—Kamote (sweet potato)—Biga—Ubi (yam)—Tugi (yam)—Lima-lima (yam)—Aroro (arrowroot)—Kamoting-kahoy (cassava).

Reviews.

HYDROGEN IONS. THEIR DETERMINATION AND IMPORTANCE IN PURE AND INDUSTRIAL CHEMISTRY. By HUBERT T. S. BRITTON, D.Sc., etc. Pp. 515. Chapman & Hall. 1929. 25s. 0d.

During recent years many attempts have been made to correlate the hydrogen-ion concentration of a system with its physical, chemical or even physiological behaviour. In some cases, no doubt, the connexion was rather forced, and the over-estimation of the importance of these ions may have justified, to some extent at least, a well-known sceptic in calling them Hydrogen Ikons! But at the same time it cannot be denied that a study of hydrogen-ion concentrations has thrown a considerable amount of light on many reactions both of analytical and of technical importance, with the result that analytical chemistry and industry have benefited to a valuable extent. Naturally the interest in the subject thus aroused has brought forth a certain amount of literature, but this has dealt more with the theoretical side, and there has hitherto been no reasonably comprehensive account of the practical aspects of hydrogen-ion concentrations.

In the book under review Dr. Britton has "endeavoured . . . to provide a practical discussion of the . . . methods of determining the concentration of hydrogen-ions, . . . to show their fundamental importance in general chemistry, including . . . analytical procedures; and . . . to indicate the important rôles played by hydrogen-ion concentrations in numerous industrial technical processes." There is no doubt that Dr. Britton has attained his objectives, and has made a valuable contribution to the literature of hydrogen ions. The first fourteen chapters of the book deal with the theory and practice of the methods of determining hydrogen-ion concentrations, including the "principles of volumetric analysis," then follow four chapters on the precipitation of hydroxides and basic salts. The last sixteen chapters are devoted to a discussion of the importance of hydrogen-ion concentrations in various industrial processes, *viz.* electro-deposition of metals; leather, sugar and paper manufacture; milk, brewing and baking industries; ceramics; etc. This latter part of the book will probably prove the most valuable, as the material contained in it has been collected from a large number of sources difficult of access. Dr. Britton does not deal separately with the subject of enzymes, although one might have expected such a treatment in view of the important contributions of Sørensen and his co-workers; various enzymes are, however, discussed in connection with technical processes.

It may, perhaps, be regarded as carping to criticise such an excellent book, but two or three points cannot be passed over. In the first place, the author does not appear to realise (p. 39) that the methods of determining P_H almost invariably gives a measure of the hydrogen-ion *activity* and not the concentration; the P_H scale as ordinarily used is, therefore, really an activity scale. Several

pages are devoted to the Ostwald theory of indicators but, as Dr. Britton points out, this is inadequate to account for their chemical properties; an important equation is deduced, however, on the basis of this discarded theory, and the point is not emphasised that the same equation can be deduced from the more complete modern theory. In the opinion of the reviewer the one-sided criticism of Werner's theory is somewhat out of place in a book of this type. The bi-valency of the mercurous-ion was established over thirty years ago by Ogg, and hence it is somewhat disappointing to find it still written as Hg^+ instead of Hg_2^{2+} .

Although the publishers have done their work quite satisfactorily, and the book is well produced, a number of misprints have been noted; but the difficulty of proof-reading the book must have been very great. In spite of the criticisms mentioned above this book may be warmly recommended to all who are interested in the subject of hydrogen ions.

S. GLASSTONE.

BACTERIOLOGY. By FRED WILBUR TANNER. Pp. xvii+548. Chapman & Hall. 1929. Price 22s. 6d. net.

As the author says in his preface, this book has been planned for those who are studying microbiology for the first time. His endeavour has been to present the whole field of bacteriological science to the reader without unduly emphasising any particular aspect, and especially without unduly emphasising the medical aspect. Moreover, his object throughout is not only to teach but to stimulate thought, and in this he has achieved considerable success, for the book is eminently thoughtful.

The scope of the book is very large, and includes the following topics:—History, Systematic Relationship; The Cell; Morphology; Chemical Composition; Classification; The Moulds; Yeasts; Protozoa; Action of Physical Agents; Relation of Chemical Agents (Disinfection); Mutual Relationship (Symbiosis, etc.); Nutrition; Growth; Enzymes; Nitrogen, Sulphur and Carbon Metabolism; Bacteriology of Air, Water, Sewage, Milk, and Dairy Products; Industrial Fermentation; Food Preservation; Illness caused by Foods; Relation of Bacteria to Disease; Transmission of Infection; Factors Influencing Infection; Modes of Bacterial Action; Protective Substances—Immune Bodies; Theories of Immunity; Varieties of Immunity; Bacteria in Plant Diseases; and Appendix, containing topical outlines for lectures and discussions, a list of publications in bacteriological literature and other useful matter.

It is obvious that with so large a scope no great detail can be expected; nevertheless, when occasion demands, the author goes into considerable detail, as, for example, when he devotes three whole pages to the exposure of the fallacious term "ptomaine poisoning." The book contains a surprising amount of useful information, such as the instructions from the Illinois Department of Public Health

for the sterilisation of water on a small scale with chloride of lime, a good description of the food-canning industry, a good account of botulism and precautions to be taken (four simple expedients) to guard against poisoning by *B. botulinus* from canned foods. One is pleased to see that the excretal and non-excretal types of *B. coli* are distinguished and tests given for their differentiation.

In the chapter entitled Relation of Bacteria to Disease a very useful summary of the characteristics of some twenty common diseases is given. The chapter on Factors influencing infection is good, the rôle of vitamins in maintaining resistance to infection receives attention, and in the paragraph on furunculoses the old-fashioned treatment by poulticing is given the condemnation it deserves.

The section on Food-borne Infections is very disappointing, except as regards botulism. Following the old erroneous German school, the author fails to distinguish *Salmonella Schottmülleri* (*B. paratyphosus B.*) from *Salmonella Aertrycke* or from *Salmonella Supestifer*, though in the references given at the end of the chapter he gives Savages' "Food Poisoning and Food Infections" and Jordan's "Food Poisoning." In the past American bacteriologists have completely disregarded the classical English work on this important subject, but for several years now Jordan, and for a year or two Meyer, the leading American authorities on food poisoning, have recognised the correctness and importance of these distinctions.

Professor Tanner possesses a very pleasing and lucid style, and is to be congratulated on producing an excellent text-book on bacteriology, not only suitable for beginners, but also of considerable interest for more advanced students. The publishers are also to be congratulated on their part; the book is well printed and very free from printers' errors.

D. R. WOOD.

THE PYROLYSIS OF CARBON COMPOUNDS. By CHARLES DEWITT HURD. American Chemical Society Monograph No. 50. Pp. 807. The Chemical Catalog Company, Inc., New York. 1929. Price \$12.50.

This book is one of the numerous works issued in recent years by the American Chemical Society in the series which aims at producing a number of volumes, each of which shall be a complete book of reference for some particular subject. In compiling "The Pyrolysis of Carbon Compounds" the author has followed the general scheme of the series. He has with great thoroughness ransacked the monumental works of Beilstein and Richter, and made free use of the journals and abstracts issued by the various chemical societies of the world. In this way he has gathered together a large number of facts which may be classed under the heading of the action of heat on carbon compounds. With consummate skill he has welded his data into a very interesting, although somewhat bulky, volume. The term "Pyrolysis" is used to cover any chemical change brought

about by heat. Thus, in addition to mere decomposition, he includes polymerisation and its converse, isomeric change, etc., but purely catalytic effects are omitted as being beyond the scope of the work.

The book opens with a chapter on generalisations which have emerged from a survey of the literature. Under this heading the rules of Least Molecular Deformation, of Bredt and of Blanc, Nèfs' Theory and the Principles of Electronic Attraction are stated. Each of these is illustrated by numerous examples, and is discussed in a critical spirit.

The remainder of the book is divided into sections under the headings of the various types of organic compounds. The following is a random selection of the subjects dealt with:—Aliphatic hydrocarbons, cyclic hydrocarbons, petroleum, rubber and related hydrocarbons, amides, anilides, hydrazides, and amino acids. Each of the subjects dealt with is amply illustrated and, where possible, generalisations are drawn.

From the nature of such a book easy reading is not to be expected, yet the author has succeeded in making his work very acceptable. Now and again the reader comes across some very interesting or suggestive fact. Thus due mention is made of Faraday's little-known contribution to the chemistry of rubber—so far back as 1826 (when he was working out the laws of electrolysis) he determined correctly the composition of caoutchouc ($C_{10}H_{16}$); and Klason's work on "the distillation of wood in a cathode light vacuum" suggests that fruitful research might be prosecuted by dealing with other organic "pyrolyses" at extremely low pressures. Or again, mention of Neuberg's interesting experiments in connection with the origin of petroleum, in which he heated together oleic and valeric acids and obtained an optically active product which gave the cholesterol test, assuredly suggests matter for further research. Similar instances, too numerous to mention, occur throughout the text.

There is very little in the book which is likely to call forth any adverse criticism, but the statements (p. 742) in the paragraph concerning Chinese wood oil (tung oil) are not in accordance with Böeseken's work on elaeostearic (elaemargaric) acid (*Rec. Trav. Chim. Pays-Bas*, 1927, 46; cf. also *ANALYST*, 1928, 53, 54, 75).

In comparison with the vast mass of well-written and interesting material contained in this book, the minor error mentioned above is of little importance. The author is to be congratulated on the able manner in which he has dealt with a very difficult and hitherto scattered subject. He has produced a rare thing—a readable reference book. The extent to which it is a reference book can be gauged by the fact that it contains two indexes (subject and author) covering 52 pages and, at a guess, considerably more than 3000 references to original memoirs. The other features of outstanding merit can be judged only by actual reading. In short, "The Pyrolysis of Carbon Compounds" is well worth the attention of all those interested in organic chemistry.

HAROLD TOMS.

RECENT ADVANCES IN HAEMATOLOGY. By A. PINEY, M.D. Second edition. Pp. x+318. London: J. & A. Churchill. Price 12s. 6d. net.

The pathologist of fifty years ago was a master of all branches of his subject. With the growth of knowledge in recent years specialisation has been inevitable, and morbid anatomists have become separated from bacteriologists and biochemists. In this book Prof. Piney has followed the modern tendency and limited its scope to the purely morphological aspect of haematology, and has omitted serology and chemistry entirely. In no other book of its size, however, is there anything giving so good a description of the morbid anatomy and histology of the blood and blood-forming organs.

After a discussion of the development of blood cells, the various blood diseases are described in detail. The changes found in the blood in various other diseases are shortly described, and finally five chapters are devoted to a consideration of various forms of splenomegaly. Three valuable appendices complete the book. The first is devoted to technique, and is an extremely useful chapter. Instead of describing numerous methods the author only describes the one he uses himself for each particular examination. In this way in a dozen pages we have a full description of all essential haematological processes instead of a brief mention of numerous alternatives. The second appendix gives a list of text-books and monographs for further study. They are chiefly German, and although "only books reposing on my own shelves have been included," they number over 100, and should be sufficient for anyone to start with. The third appendix is a glossary of terms, a most necessary part of any book on haematology, with its enormous nomenclature.

From cover to cover the book expresses the personal opinions of the author, and is entirely different from so many American monographs, which seem to be prepared by the "scissors and paste" method without any attempt at digesting the fragments. This, of course, has the disadvantage of personal bias, and also that certain aspects of the subject are barely mentioned; for example, the work of Price Jones on the size of red blood cells and the methods of Pijper and others for measuring them by the halometer. Nevertheless, the fact that it has had a second edition within a year of the first is sufficient evidence that the book has filled a gap in haematological literature, and it can be warmly recommended as a useful text-book.

W. D. NEWCOMB.

VOLUMETRIC ANALYSIS. Vol. II. **PRACTICAL VOLUMETRIC ANALYSIS.** By I. M. KOLTHOFF, with the collaboration of H. MENZEL. Authorised translation from the German by N. H. FURMAN. Chapman & Hall. Pp. 552. Price 25s.

This book completes the translation into English of Kolthoff's important work on Volumetric Analysis; the German original of this section of the work has

already been reviewed and a summary of its contents given (ANALYST, 1929, 257). The translation contains some fifty additional pages, supplied by Kolthoff, of new matter dealing with methods which have been devised and improved since the book was first written; the new material includes a chapter on the use of ceric sulphate as a volumetric reagent. When describing the German original the reviewer stated that this book was not for the beginner in volumetric analysis, and it would be as well to emphasise the fact once more; the book, however, contains an excellent critical survey of a large number of interesting methods, and a study of the work should well repay even an experienced analyst.

The English translation of Volume II suffers from the same defects as does that of the first volume (see ANALYST, 1929, 194); Dr. Furman has attempted a too literal rendering of the German, and consequently, as well as for other reasons, the English style has suffered. On page 98 is found the statement "we . . . have arrived at somewhat different results than Incze," and on page 299 we read, "Also in acetic acid solution at boiling, thiosulphate is only incompletely oxidised, even in a long time, according to Höning and Zatzek." Apart from the occasional "roughness" of the English, the translation has been well done, and the work is singularly free from misprints; the most serious error noted was "hypochloric" for "hypochlorous" acid (page 311).

It should be mentioned that the normal potentials for chlorine, bromine and iodine, quoted on page 385 (also on page 370 of the German edition) are incorrect, although their order, which is really the important point, is correct. Curiously enough, the values for these electrode potentials are given correctly at the end of Volume I of this work.

S. GLASSTONE.

Publications Received.

LAW AND INDUSTRY. By G. S. W. MARLOW, B.Sc. F.I.C. London: Baillière, Tindall & Cox. Price 18s.

GASEOUS COMBUSTION AT HIGH PRESSURES. By W. A. BONE, D.Sc., F.R.S., D. M. NEWITT, Ph.D., and D. T. TOWNEND, Ph.D. London: Longmans, Green & Co. Price 42s. net.

A TEXT-BOOK OF BIOCHEMISTRY. By A. T. CAMERON, D.Sc., F.I.C. 2nd Edition. London: J. & A. Churchill. Price 15s.

CHEMISTRY IN DAILY LIFE. By S. GLASSTONE, D.Sc., F.I.C. London: Methuen & Co. Price 6s. net.

THE ANALYST

PROCEEDINGS OF THE SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

AN Ordinary Meeting of the Society was held at the Chemical Society's Rooms, Burlington House, on Wednesday, November 6th, the President, Mr. Edward Hinks, being in the chair.

Certificates were read for the first time in favour of:—Noel Lionel Allport, A.I.C., James Gilbert Lunt, B.Sc., A.I.C., Fred Morris, F.I.C., Albert William Peters, Juda Hirsch Quastel, D.Sc., Ph.D., A.R.C.S., A.I.C., and Joseph Harold Totton, B.A., B.Sc., F.I.C.

Certificates were read for the second time in favour of:—Alfred George Avent, A.I.C., William Rhys Davies, F.I.C., Ernest Roadley Dovey, A.R.C.Sc., F.I.C., James Gray, F.I.C., James Henderson, B.Sc., A.I.C., Claude Alexander Scarlett, B.Sc., A.K.C., A.I.C., Percy Arthur William Self, B.Sc., F.I.C., Thomas Brooks Smith, B.Sc., A.R.C.S.

The following were elected Members of the Society:—John William Haigh Johnson, M.Sc., F.I.C., Mamie Olliver, B.Sc., A.I.C., and George Edw. Shaw, B.Sc.

The following papers were read and discussed:—"The Grouping of Fatty Oils with Special Reference to Olive Oil," by E. R. Bolton, F.I.C., and K. A. Williams, B.Sc., A.I.C.; "The Heat-Resistance Curve: A New Bacteriological Test for Pasteurised Food," by Cuthbert Dukes, M.D., M.Sc., D.P.H.; and "A New Borax Solubility Test for Lactic Acid or Natural Sour Casein," by W. R. Mummery, F.I.C., and F. Bishop.

Death.

WITH deep regret we record the death, on November 13th, of Dr. Samuel Rideal, a Past-President of the Society. An obituary notice will be published in a subsequent issue.

The Chemical Examination of Furs in Relation to Dermatitis.

By H. E. COX, M.Sc., Ph.D., F.I.C.

(Read at the Meeting, October 2, 1929.)

CASES of dermatitis, attributed to the wearing of dyed furs, have occurred with increasing frequency during the last few years; many, perhaps most, have been well authenticated, and the clinical diagnosis certain, but in others, although the dermatitis may be beyond question, it is open to doubt whether it has originated from the action of anything toxic in the fur. There is now quite a considerable literature on fur dermatitis, but, so far as I am aware, there is little published information on the analytical side; and some of the statements bearing on this aspect of the matter are not in agreement with my observations, which are based on the examination of quite a large number of furs alleged to have caused the disease.

Two medical papers dealing with the causes and symptoms of fur dermatitis are of particular interest: Dr. Prosser White's (*Trans. Lond. Dermat. Soc.*, 1923, p. 41), and Dr. Parson's Report to the Minister of Health (No. 27 of 1924); the latter has a bibliography up to the year 1924. Briefly put, the cause of dermatitis with which we are concerned is the presence in or on the fur of active chemical substances used in the dyeing process; these may remain as the result of incomplete oxidation in the dye-forming stage or incomplete washing afterwards. Arsenic, lime and various inorganic substances used in preparing the skins have been known to occasion disease to workers in the factories, although there appear to be no recorded cases in which dermatitis to the wearer has been traced to such substances. The possibility of such action needs to be borne in mind in the examination of a fur if it is found not to have been dyed, or is one which yields no reaction for the organic compounds usually concerned.

DYEING PROCESSES.—These organic compounds are the irritant dyes or intermediates used in dyeing fur by oxidation or developing processes in which the

pigment is produced in or on the fur by immersion in a bath containing the intermediates, with hydrogen peroxide, potassium chlorate, dichromate or vanadium compounds as oxidising agents. Alternatively, the colouring may be effected by brushing the ends of the fibres with the appropriate solutions; this method is useful where it is desired to tint the hair rather than dye the whole skin. More recently all kinds of finished dyes, acid, basic and chrome, have been employed, and the use of vat dyes has lately been advocated. Such dyes are not so likely to be irritant to the skin as are those dependent on development by oxidation on the fur. It is not always easy to say whether a fur has been dyed, and careful examination must be made of the hairs and of the skin as a whole, for it sometimes happens that only part of the fur on a collar or other garment has been dyed, or that it has been dyed in stripes with different substances; and sometimes in a coat made up from pieces of small skins, some of the pieces are heavily dyed and contain the irritant substances, whilst other pieces do not. Clearly, one is mainly interested in those parts of the fur which would come in contact with the face, neck or wrists of the wearer.

CHARACTERISTICS OF FURS.—It is useful to examine the specimen both macroscopically and microscopically to determine if possible what kind of fur it really is, and whether it has been dyed. The most common is the rabbit, which appears under a variety of names which do not suggest the genus *Lepus*. Illustrations of a few types are to be found in Mitchell and Prideaux's book, *Fibres Used in Textile and Allied Industries*, and in an article by the same authors in *Knowledge* (1910, 36, 283). Verbal descriptions and even photographs are of limited utility for the identification of hairs of different mammals, but the following account may be given of some of those most frequently met.

The long fully-developed hairs of the fur are of the greatest diagnostic interest. It is curious that in nearly all furs there is a sort of substratum of short wool-like hair having but little medulla; these hairs do not present any marked differences in the different animals; so the long, fully developed, fibres should be examined, or an erroneous deduction may be made. The descriptions given apply to the fully developed hairs. It is possible that other animal hairs may present similar features, but I have not observed any, other than the rabbit and hare, which show the characteristic longitudinal marks found in rabbit fur.

Rabbit.—These are mainly small fibres about 2 cm. in length and 30–40 μ diameter. Some are as wide as 80 μ , and show 3, 4, 5, or 6 rows of medullary cells with well-defined longitudinal lines; the medullary cells in the larger hairs occupy almost the whole thickness. (Fig. 1.)

Hare.—These are similar to the rabbit hairs, but are longer and thicker. The hairs may be 3 cm. or more in length and 100 μ diameter, but show the characteristic medulla.

Cat.—These hairs are generally smaller than those of the rabbit; length about 2.5 cm. and width 15–35 μ . The medullary cells are rectangular and some

distance apart; they do not occupy the whole width as in the rabbit. The edge shows scales distinctly. (Fig. 2.)

Peschianiki (Russian Cat).—This fur differs materially from that of the ordinary cat. The fibres, though short and soft, are much thicker (about $100\ \mu$ in the largest), and the medulla occupies most of the width, and is composed of thin-walled cells compressed in concertina fashion; the appearance is not unlike the scales of a fish in the wider hairs. (Fig. 3.)

Opossum.—Large thick hairs, 3–5 cm. long and 50 to $80\ \mu$ wide. They are fairly uniform, and have a thick medullary layer occupying about half the width. The medullary cells are thick and distinct in outline. (Fig. 4.)

Skunk.—This shows hairs wider than the opossum, and with a very wide, ill-defined medulla, not showing definite cell walls; length 5 or 6 cm. The smaller hairs are much scaled, and generally there is more woolly hair at the base of the fur than with the opossum. (Fig. 5.)

Nutria (Coyou or Otter).—Short woolly fibres about 2 cm. long and $20\text{--}30\ \mu$ diameter, showing large scales but no medulla; fairly uniform. (Fig. 6.)

Sable (Weasel).—These are rather delicate hairs, though large. The width is up to $80\ \mu$, with a wide dense medulla interlocked with cells showing scale-like markings. The small hairs show barbed scales at the edge. (Fig. 7.)

Fox.—The fur has long hairs (6 or 8 cm.) with bearded edges; the width is about $50\ \mu$, and there is a dense thick-walled medulla occupying 80 per cent. of the width. (Fig. 8.)

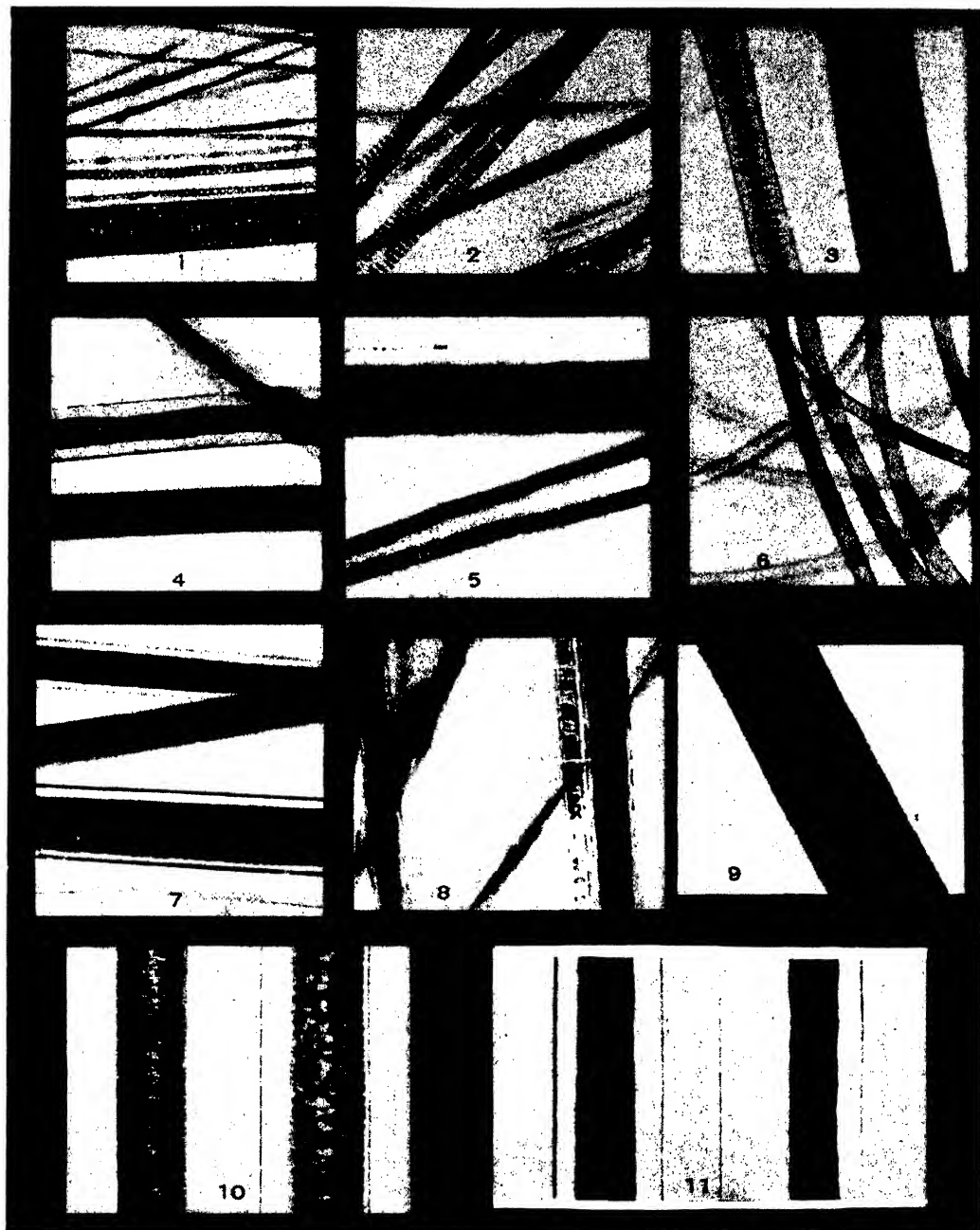
Goat.—The hairs are long and coarse and very dense; length up to 6 cm., and width 120 to $130\ \mu$. The medulla is thick, occupying 75 per cent. of the width, and has a fishscale-like structure. (Fig. 9.)

Wallaby.—The hairs are about 3 cm. in length and $80\ \mu$ in diameter; well defined, dense medulla occupying nearly the whole width, irregularly arranged cells not overlapping, as do those of the weasel; smooth edges. (Fig. 10.)

Raccoon.—The fur has long coarse hairs, 5 or 6 cm. by $120\ \mu$; very dense medulla, $50\ \mu$ wide, with smooth edge and indefinite structure; the sheath of the hair is smooth and transparent, showing no scales. (Fig. 11.)

COMMON IRRITANT DYESTUFFS.—While the number of dyestuffs or intermediates which may be applied to furs is quite large, the following is a list of the more common and possibly irritant ones:—(1) meta-phenylene diamine; (2) para-phenylene-diamine; (3) toluylene-diamine 1:2:4; (4) toluylene-diamine 1:3:4; (5) toluidine *o*-, *m*- and *p*-; (6) pyrogallol; (7) quinone; (8) hydroquinone; (9) para-aminophenol (ursol P.); (10) di-aminophenol (amidol); (11) para-methyl-aminophenol (metol); (12) di-amino-diphenylamine. It is my purpose to describe tests which are available for these substances in dilute solution. The list is not

TYPES OF FIBRES IN FURS.



- | | | | | |
|---|---------|----------------|------------|----------|
| 1 Rabbit. | 2 Cat. | 3 Russian Cat. | 4 Opossum. | 5 Skunk. |
| 6 Coypou. | 7 Sable | 8 Fox. | 9 Goat. | |
| 10 Wallaby (two parts of the same fibre). | | | | |
| 11 Raccoon (two parts of the same fibre). | | | | |

exhaustive, but it is readily demonstrable by physiological experiment that all, except No. 5, are definitely irritant to the skin. Nos. 1, 2, 3 and 6 are, in my experience, the most common, and, of these, para-phenylene-diamine is perhaps the most frequently met with, and the most toxic. With regard to toluidine, I do not think it likely that it is irritant in small quantity to the normal skin, and certainly, when applied to my own arm, it did not produce any inflammation in 24 hours, although para-phenylene-diamine does so in an hour or two, and diamino-phenol raises blisters which persist for days. It sometimes happens that two of these substances may be present in the same fur, as in the case of one (exhibit) showing stripes of brown and black, due to pyrogallol and *m*-phenylene respectively. Methoxy and ethoxy groups may be associated with para-phenylene-diamine, and naphthalene-diamines are a possibility.

All these substances are strong reducing agents and reduce silver nitrate; several are known as photographic developers, some of which cause irritation and blisters on the fingers of persons with sensitive skins. They also reduce Fehling's solution, with the production of various colours, but these colours are not sufficiently constant for diagnostic purposes, being much influenced by concentration and by other substances which may be extracted from the fur.

IDENTIFICATION REACTIONS.—The following reactions all apply to aqueous solutions in concentration 1 in 10,000; they are distinctly visible at this concentration, and many of them at 1 in 100,000, some even at greater dilutions, especially if viewed in column in Nessler glasses. They are sufficient for the identification of the substances named, though I cannot state definitely that the colours are absolutely specific in all cases. It is needful to confirm the reactions and not take one test as conclusive; thus the yellow colour with sodium nitrite is given by several other substances besides the commonest one—meta-phenylene-diamine; and, of course, there may be a mixture of two or more substances which will complicate the reactions. Care must be taken not to add too much reagent, especially when testing very dilute solutions. In the case of test (4) it is important that the solution should not contain any free acid, or chlorine may be liberated and a different reaction obtained; the solution should be neutral or very slightly alkaline, and large excess of hypochlorite must be avoided, or the colour may be bleached. This test is not equally valuable in all cases; for example, the difference between the brownish-pink given by meta-phenylene-diamine or 1:2:4 *m*-toluylene diamine and the violet-blue of para-phenylene-diamine and 1:3:4 meta-toluylené diamine is distinctive, but, though the three toluidines give different colours when pure, it is not practicable to distinguish them in very dilute solution as extracted from fur.

In test (5) the solution should be distinctly acid with hydrochloric acid; this reagent, which is the familiar indole reagent of the bacteriologist, serves to distinguish *p*-phenylene-diamine from meta-toluene-diamine. In No. 6 about 2 drops of ferric chloride solution should be added to the neutral or faintly acid

liquor, then hydrogen sulphide water, 1 c.c. at a time; a large excess may mask the colour or liberate sulphur.

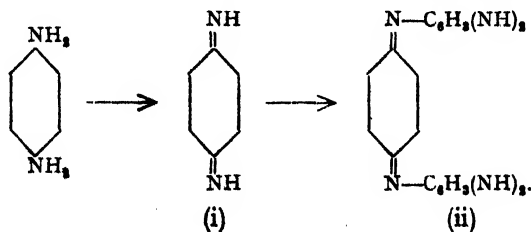
The reduction of Fehling's solution in the cold refers to the effect observed on adding 3 or 4 drops of mixed Fehling solution to 5 c.c. of the solution to be tested, not to the reverse addition of a little of the solution to be tested to a relatively large volume of the Fehling solution. It is generally advisable to use boiled cooled distilled water to eliminate oxidation as far as possible, and the solutions should be fairly fresh.

	Meta-phenylene-diamine.	Para-phenylene-diamine.	1:2:4-Meta-toluylene-diamine.	1:3:4-Meta-toluylene-diamine.	Para-amino-phenol.	Para-amino-diphenylamine.
1. Dilute sodium nitrite added to cold acidified solution.	Intense brownish yellow	Slight* brown colour (fades)	Orange colour	Brownish pink	Slightly yellow	Red
2. Excess of alkaline solution of β -naphthol added to (1).	Reddish-brown colour	Brownish colour	Intense red	Dirty yellow or brown	Fluorescent green afterwards turning brown	Yellow or brown
3. Bromine water.	Slight white ppt.	Nil	Nil	Very faint ppt.	Nil	Brownish precipitate
4. Phenol (5 per cent. solution) and 2 drops of sodium hypochlorite added to neutral solution.	Pink	Violet blue	Pink	Violet	Blue	Yellow colour
5. Alcoholic solution of <i>p</i> -dimethyl-amino-benzaldehyde added to acidified solution.	Bright yellow	Red	Yellow	Yellow	Yellow	Faint yellow
6. Ferric chloride.	Nil	Violet	Nil	Violet	Nil	Reddish violet
7. Hydrogen sulphide water added to (6).	Nil	Intense violet	Nil	Claret colour	Violet	Brick-red colour
		The dimethyl compound gives similar reactions but a blue colour with FeCl_3 and H_2S . Both give a pink colour with potassium cyanide.	Reduces Fehling's solution in the cold			Violet colour with quinone

* As this cannot be a real diazo compound, it is probably an oxidation reaction.

	<i>o</i> -, <i>m</i> -, <i>p</i> -toluidine.	2:4-Diamino-phenol.	Methyl- <i>p</i> -amino-phenol.	Quinone.	Hydro-quinone.	Pyro-gallol.
1. Dilute sodium nitrite added to acidified solution.	Nil	Bright red	Faint yellow	Nil	Faint yellow	Nil
2. Excess of alkaline naphthol added to (1).	Bright red colour or ppt.	Brown colour	Slightly brown	Slight reddish colour	Red colour	Nil
3. Bromine water.	White ppt.	White ppt.	Nil	Nil	Nil	Nil
4. Phenol (5 per cent. solution) and 2 drops of sodium hypochlorite added to neutral solution.	Brown at first, <i>o</i> - and <i>m</i> -subsequently become blue	Red colour	Blue-violet develops slowly	Nil	Nil	Brownish
5. Alcoholic solution of <i>p</i> -dimethyl-amino-benzaldehyde (acidified).	Greenish yellow	Yellow	Nil	Slight yellow	Slight yellow	Slight yellow
6. Ferric chloride.	Nil	Nil	Nil, but turns green on adding H_2S	Nil	Nil	Reddish, turning greenish-black
7. Mercuric acetate solution.	Nil	Purple colour	No colour (very slight pink on standing)	Pale yellow with mercuric sulphate	Nil	Yellowish
8. Potassium cyanide solution.	Nil	Greenish blue	Yellow slowly develops	Brownish Reduces Fehling's solution cold. Gives purple-black colour with ammoniacal copper chloride, also violet colour with <i>p</i> -amino-diphenylamine	Yellow	Pink Gallic acid gives bright red with mercuric acetate

OXIDATION PRODUCTS.—The chemistry of the oxidation of these substances is obscure, and the composition of the final products appears to be unknown. Paraphenylene-diamine is of particular interest in this connection, because of the intermediate compounds formed during its oxidation and their possible toxicity. It seems certain that the first stage (according to Prof. Perkin) is the formation of quinone di-imide (i), and the second Bandrowski's base (ii) thus:



Some controversy centres round this substance. Gordon (*Trans. Med.-Legal Soc.*, 1926, 20, 73) shows that it is non-irritant and expresses the opinion that it is the proper end-product in fur dyeing. This seems to be open to question, as, although the constitution of finished black or brown (in its many forms) is not settled, it is clear that it has at least 8 rings, and that Bandrowski's base is not the final product, nor is it a fast colour. Gordon attributes the irritant properties of fur dyed with para-phenylene-diamine to a substance which he calls "A", the constitution of which is not stated, but which gives a coloured solution with water, whereas the base B. is insoluble; it would appear that A. is the di-imide. He identifies A. by spectroscopic comparison. In my observation of these dyes and their intermediate products there is only a general absorption visible spectroscopically, not a specific one, so that one cannot differentiate with certainty the colour due to A. from that of other (possibly similar) bodies, or even some finished dyes. It may further be remarked that Bandrowski's base is easily reduced to the form of a leuco compound (*Ber.*, 1894, 27, 482), so that it may, in appropriate circumstances, be an indirect cause of irritation. In my experience, Bandrowski's base is always associated with some partially oxidised para-phenylene-diamine, which can be detected by the reactions given.

EXTRACTION OF THE FUR FOR THE TESTS.—For the application of these tests extracts from the fur must be prepared; this may be done by cutting the fur from the skin as closely as possible (sometimes it is desirable to soak the skin also), de-fatting with petroleum spirit, then extracting with (1) cooled boiled water, (2) dilute (1 per cent.) acetic acid for at least 24 hours. All the solutions should be preserved from atmospheric oxidation as much as possible. The petroleum spirit should be shaken with acidified water to extract from it any bases. The object of using weak acetic acid is to simulate the action of perspiration, which in contact with the fur may be an agency in setting up the irritation. Some furs which are easily wetted may be soaked without de-fatting.

The extract so prepared should be tested for inorganic substances and for acids, as well as for dyestuffs or intermediates. Well-dyed furs yield no colour when so treated, other than a trace of dirt; those containing diamines are usually of a distinct brown or pink colour, which is an unfavourable sign. Decolorisation of the extract with charcoal is inadvisable, as it may remove traces of the important substances.

It is interesting to make an approximate estimate of the amount of any substance detected in the extract; this can be done colorimetrically by comparison with known solutions, using the same volumes of reagents. The question of what quantity is deleterious is beyond the scope of this paper. The worst case in my observation contained about 20 mgrms. of para-phenylene-diamine in 1 grm. of fur (including the skin), which was equivalent to an area of about 6 square inches: usually very much less is found, and sometimes a trace so small that it is open to doubt whether it could possibly cause dermatitis to a normal person, and in such

cases practical physiological test, in the manner described by Dr. Gordon, is particularly valuable.

I wish to thank Mr. T. J. Ward for kindly preparing the photo-micrographs for me.

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DISCUSSION.

The PRESIDENT said that this matter had been before chemists for a good many years, and this was the first systematic attempt they had had to deal with the problem (and, he thought, the first mention in *THE ANALYST*). The Society was very much indebted to Dr. Cox for the work and the information he had given them. It was a strange thing, seeing how largely articles of clothing were dyed, that this trouble occurred only with fur; he presumed there were particular difficulties in the dyeing of fur. He was sorry that Dr. Gordon could not be present, as he was particularly interested in this subject. He thought that Dr. Gordon's spectroscopic tests had been done on what he (Dr. Gordon) described as "Material A," and not on "Material B."

Dr. ROCHE LYNCH referred to a case he had seen of a substance for tinting eyebrows and eyelashes, which had caused intense dermatitis. He regarded the main issue as being the fact that one could prove that any one of this group of substances was present (not necessarily identify it); to be able to extract it was practically to condemn a fur in a case of dermatitis. Dr. Cox had suggested that possibly the size of the individual fibres might cause irritation, and Dr. Roche Lynch would suggest that the one most likely to produce that effect was fox; it had been clearly pointed out that these hairs had very large natural spines. He asked whether the same group of substances was used in dyeing serges and cloth, and, if so, whether the author had come across any cases of irritation caused through black serge or black cloth. If not, there must be two factors—one dye and one the actual fibre of the fur.

Mr. W. PARTRIDGE pointed out that references to papers on the subject by Semon, Roxburgh and Castle had appeared in *THE ANALYST* for 1923 (pages 282, 283 and 284, respectively). He referred to cases where mineral substances, notably chromium compounds and also salt, had been the causes of dermatitis from furs.

Mr. F. W. F. ARNAUD said that the paper was of very great importance, because, from time to time, chemists were called upon to examine furs alleged to have caused dermatitis. It was probably well known that some people suffered from severe irritation from the mere presence of flannel next to the skin. He enquired whether Dr. Cox had tried any method of concentrating the intermediates, because, if this were possible, the reactions would be more marked and differentiation of injurious substances would be easier. He referred to a case where a dog suffered from dermatitis round the neck, which was found to have been caused by a collar made of chrome leather.

Mr. R. L. COLLETT said that it was possible to identify a number of animals by the surface of the skin and the arrangement of the hair follicles in it—he instanced goat. It would be very interesting to see whether these fur-bearing animals had any particular arrangement of the follicles. Dr. Roche Lynch had

pointed out the possibility of the fibre itself being an irritant. The hairs, for instance, of the wild boar which was used in brush-making had a distinct serrated surface. Hair was not an absolutely inert substance, and he thought that in all these examinations of hair one should bear in mind that it was possible that substances were being extracted from the hair itself which might have an important bearing on the results.

Dr. C. A. MITCHELL agreed with the caution given by Dr. Cox, when he pointed out that more than one type of hair might occur in a fur. Fibres ranging from the woolly type to the characteristic hair type were common in the fur of most animals, and good examples of both types could be found in the coat of the Bedlington terrier. He suggested that the osmium tetroxide reaction for pyrogallol, which he (the speaker) had devised and adapted to quantitative purposes (ANALYST, 1924, 49, 162) might be of service in determining pyrogallol in the very dilute extracts from dyed furs. In one instance where a claim had been made he had found that the extract from the fur gave a coloration which corresponded with 1 part of *m*-phenylene-diamine in 20,000 parts of the pelt. This claim was settled out of court.

Dr. J. T. DUNN congratulated Dr. Cox. He said that he had had very little experience himself of fur dermatitis. In one or two cases, however, he had found that dermatitis was not due to dye at all, but to potassium chromate.

Mr. C. E. SAGE said that these analytical tests required very careful consideration. With regard to the cause of dermatitis, he did not know that chemists had anything more to do than to express personal opinions. He then referred to the fact that some people possessed exceedingly sensitive skins which were affected where others were not, and illustrated this with examples from his own experience.

Prof. J. T. HEWITT (in a written communication) said that it seemed that there was no case for the actual dyeing of fur by Bandrowski's base; the oxidation was carried out on the fibre, and there was nothing to show that the fur itself did not also take part in the reaction. He thought that a pigment of the aniline-black type was probably present, and referred to papers by Erdmann (*Ber.*, 1904, 37, 2776, 2906) and by Heiduschka (*Arch Pharm.*, 1916, 254, 584), showing that the oxidation of *p*-phenylene-diamine gave different results according to the oxidising agent employed.

Dr. Cox, replying, said that, having no experience of the practice of dyeing cloth, he could not answer the questions on this point. With regard to irritation due to non-dyed furs, he thought that when these cases come to the analyst they were usually in relation to a claim for money; if there was nothing improper or irritant on the fur, it did not seem reasonable that the vendor or merchant should be called upon to pay because a wearer happened to have super-sensitive skin. If, however, a known toxic substance could be identified it would be difficult to avoid liability.

It appeared to be necessary to dye furs in alkaline or half-alkaline* solution, because acid or acid liberated from hydrochlorides tended to rot the fibres. He had tried to concentrate the solutions of extract from the fur, but found that oxidation took place, which might spoil the tests. In reply to Mr. Hinks, he found that the absorption spectrum (at least in the visible region) of the substance A and of most of the intermediates was general not specific, and was not of much diagnostic value.

* *I.e.*, with one of the HCl groups of the hydrochloride neutralised.)

ADDENDUM BY DR. KNYVETT GORDON.

My own contributions to the subject are summarised in a paper read before the Medico-Legal Society in March, 1926. Prior to this, I had described in March, 1924 (*Medical Press and Circular*, March 26th, 1924) some experimental work on the effect of certain dyes on human skin, and the report of the Ministry of Health was issued in September of the same year, but contained no reference to these experiments.

The Ministry attributed the deleterious effects of certain furs in regard to dermatitis to Bandrowski's base, but I had previously shown, by cutaneous tests (in the papers referred to), that this substance was neither poisonous nor irritating. I have frequently applied it in the fresh state to scarified human skin without any visible or sensory effect whatever.

On the other hand, the soluble intermediate oxidation products of para- and meta-phenylene-diamine are highly irritating, and I think there can be no doubt that it is to them, and not to the insoluble Bandrowski's base, that fur dermatitis is due. Inasmuch as careful washing of the fur suffices to remove these intermediate products, their presence is rightly held by the Courts to justify a claim for negligence.

I regard this contribution to our knowledge of microscopy of the various furs and the chemical tests for dyes therein as of great value; but when one is asked to decide as to whether a claim against a fur, for having given rise to dermatitis in the human subject, is justified or not, it is mainly to tests on the skin that one should turn. These, however, require careful control on the lines which I endeavoured to indicate in my paper to the Medico-Legal Society.

Dr. Cox has done much service in enlarging the list of dyes which might be incriminated in any given case, and it will now be advisable to apply the physiological test to these; but, from the practical point of view, the points that come into Court are:

- (1) Whether the patient is suffering from true fur dermatitis or one of the diseases which closely simulate it;
 - (2) Whether the patient has a natural idiosyncrasy with regard to rabbit or whatever the natural fur may be;
 - (3) Whether the incriminated fur does, or does not, cause irritation or inflammation of a normal human skin when tested by the appropriate methods.
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Investigations into the Analytical Chemistry of Tantalum, Niobium, and their Mineral Associates.

XVI. Observations on Tartaric Hydrolysis.

XVII. The Quantitative Precipitation of the Earth Acids and certain other Oxides from Tartrate Solution.

By W. R. SCHOELLER, Ph.D., AND H. W. WEBB.

(Work done under the Analytical Investigation Scheme.)

(Read at the Meeting, October 2, 1929.)

XVI. OBSERVATIONS ON TARTARIC HYDROLYSIS.

THIS Section continues the work recorded in Section I (ANALYST, 1922, 47, 93) and IX, Part II (*id.* 1927, 52, 633). In the former, a forecast is given of a scheme for the analysis of earth-acid minerals, in which the initial hydrolysis is avoided by solution of the pyrosulphate melt in tartaric acid solution; in the latter, it is shown that the tartaric solution of the earth acids undergoes hydrolytic precipitation when boiled with excess of nitric or hydrochloric acid ("tartaric hydrolysis"). The precipitate is purer than that formed in the customary pyrosulphate hydrolysis (XII, ANALYST, 1928, 53, 474), an approximate separation of the earth acids from titania being the most obvious advantage of the new process. In this Section, we submit a study of the quantitative course of the tartaric hydrolysis of the earth acids in presence of some of their mineral associates, the data being considered necessary in view of the likely application of the procedure in the proposed scheme of mineral analysis. When this is carried out as planned in Section I, the tartaric solution of the earth acids, freed from certain elements, may still contain "tungsten, titanium, and zirconium; rare-earth metals and thorium; aluminium, glucinum, manganese, calcium, and magnesium." The deportment of most of these elements in the tartaric hydrolysis is described below.

A. EARTH-ACID RECOVERY NOT QUITE QUANTITATIVE.—The recovery of the earth acids from tartrate solutions has already been illustrated in Table V, Section IX (*loc. cit.*); a small positive error, for which we have no satisfactory explanation, was observed in the two tantalum experiments Nos. 1 and 3. Such positive errors have never recurred in subsequent work; in a typical experiment, 0.2003 grm. of Ta_2O_5 gave a precipitate weighing 0.1985 grm. We are satisfied that the recovery of the earth acids is never quite complete.

Two additional tests were made with small amounts of the pentoxides, which were fused with bisulphate and precipitated from tartrate solution by 15 minutes' boiling with 30 c.c. of hydrochloric acid in a bulk of 200 c.c.:

Exp.	Taken.	HP.	Error.	Ppt. formed:
2	Ta ₂ O ₅ 0.0110 grm.	0.0100	-0.0010	after 1 minute's boiling
3	Nb ₂ O ₅ 0.0111 grm.	0.0104	-0.0007	at once

It may be stated here, in view of our contemplated work on the separation of the earth acids from the rare earths (*cf.* Pied, ANALYST, 1925, 50, 36), that hydrolytic precipitation of the earth acids from oxalo-tartaric solution is quite incomplete; hence tartaric hydrolysis cannot be applied to solutions containing also oxalic acid. In Exps. 4 and 5, one grm. of ammonium oxalate was added, and the tartaric solutions boiled as usual with 30 c.c. of nitric acid:

Exp.	Taken. Grm.	HP. Grm.	Ppt. formed:
4	M ₂ O ₅ 0.2025	0.1117	} very gradually
5	do. 0.2060	0.1289	

The use of hydrochloric (instead of nitric) acid as an alternative precipitating agent was tried in practically all the tests here recorded, because hydrochloric acid may be almost completely removed from the hydrolysis filtrate by evaporation, without destruction of the tartaric acid; with nitric acid this is not feasible. Nitric acid has the disadvantage that it destroys cupferron, a reagent likely to be used in subsequent work (*vide infra*, Sect. XVII).

B. TUNGSTEN AND EARTH ACIDS.—The similarity in the behaviour of tartaric solutions of tungsten, tantalum, and niobium towards nitric acid is brought out in Exps. 6 to 9. The tungsten precipitate is yellow and filters well. When hydrochloric acid is used, the precipitation is incomplete at higher, and may not take place at all at lower, concentrations (Exps. 10 and 11):

Exp.	Taken. Grm.	Precipitant.	HP. Grm.
6	WO ₃ 0.1000	30 c.c. HNO ₃	0.0952
7	" 0.1000	do. do.	0.0958
8	" 0.1000	do. do.	0.0934
9	" 0.1036	} do. do.	0.3000
	M ₂ O ₅ 0.2045		
10	WO ₃ 0.1000	30 c.c. HCl	no ppt.
11 ¹	" 0.3218	35 c.c. do.	0.2808

¹ 0.5 grm. of wolframite (64.36 per cent. WO₃ by *aqua regia* method) fused with bisulphate; melt dissolved in tartaric acid; boiled with HCl.

C. TITANIA AND EARTH ACIDS.—As stated in the preamble, an approximate separation from titania is achieved by the procedure. Nitric acid having been used as the precipitant in the earlier investigation (IX, *loc. cit.*, Table VI), two supplementary experiments were carried out in which precipitation was effected by 5 minutes' boiling with 30 c.c. of hydrochloric acid in a total bulk of 300 c.c. When the combined filtrates from P¹ and P² are boiled down sufficiently, a small additional earth-acid precipitate, P³, is formed; this is filtered off before

the complete expulsion of the hydrochloric acid; otherwise it re-dissolves in the residual strong tartaric acid solution:

Exp.	M_2O_5 taken. Grm.	TiO_2 added. Grm.	HP^1 . Grm.	HP^1 re-treated. Grm.	TiO_2 in. Grm.	M_2O_5 by difference. Grm.
Ta 12	0.1114	0.1128	0.1241	P^2 : 0.1076 P^3 : 0.0067	P^2 : 0.0052 P^3 : 0.0006	P^2 : 0.1024 P^3 : 0.0061
Nb 13	0.1110	0.1141	0.1381	P^2 : 0.1151 P^3 : 0.0028	P^2 : 0.0145 P^3 : 0.0002	P^2 : 0.1006 P^3 : 0.0026

It is seen that the separation of titanium from tantalum is more satisfactory than that from niobium; in Exp. 12, re-treatment of P^{2+3} yielded P^4 , weighing 0.0928 gram. and containing only 0.0010 gram. TiO_2 .

D. ZIRCONIA AND EARTH ACIDS.—Mixtures of the pentoxides and zirconia, after bisulphate fusion, were hydrolysed in solutions containing 3 grms. of tartaric acid, both by nitric and by hydrochloric acid; the precipitate, HP , was collected, washed with acidulated water, ignited, and weighed:

Precipitant: 30 c.c. HNO_3 .					Precipitant: 30 c.c. HCl .				
Exp.	Taken Ta_2O_5 . Grm.	Added ZrO_2 . Grm.	HP . Grm.	Error. Grm.	Exp.	Taken Ta_2O_5 . Grm.	Added ZrO_2 . Grm.	HP . Grm.	Error. Grm.
14	0.1009	0.0117	0.1034	+0.0025	28	0.1026	0.0123	0.1013	-0.0013
15	0.1017	0.0216	0.1040	+0.0023	29	0.1008	0.0211	0.0954	-0.0054
16	0.1008	0.0312	0.0955	-0.0053	30	0.1012	0.0314	0.0843	-0.0169
17	0.1012	0.0428	0.0856	-0.0156	31	0.1009	0.0408	0.0701	-0.0308
18	0.1030	0.0520	0.0775	-0.0255	32	0.1023	0.0519	0.0540	-0.0483
19	0.1006	0.0753	0.0584	-0.0422	33	0.1022	0.0753	0.0367	-0.0655
Nb_2O_5					Nb_2O_5				
20	0.1020	0.0121	0.1008	-0.0012	34	0.1028	0.0109	0.0984	-0.0044
21	0.1014	0.0209	0.1018	+0.0004	35	0.1018	0.0211	0.0982	-0.0036
22	0.1014	0.0322	0.0996	-0.0018	36	0.1010	0.0331	0.0967	-0.0043
23	0.1028	0.0429	0.0984	-0.0044	37	0.1025	0.0440	0.0966	-0.0059
24	0.1016	0.0531	0.0980	-0.0036	38	0.1018	0.0590	0.0947	-0.0071
					39	0.1016	0.0750	0.0985	-0.0031
M_2O_5					M_2O_5				
25	0.1037	0.0152	0.1072	+0.0035	40	0.1032	0.0142	0.1066	+0.0034
26	0.1009	0.0419	0.1070	+0.0061	41	0.1052	0.0453	0.1098	+0.0046
27	0.1018	0.0732	0.1018	0.0000	42	0.1056	0.0727	0.1002	-0.0054

The figures make it evident that the recovery of the tantalum decreases with an increase in the zirconia, whereas, curiously enough, the precipitation of the niobium is hardly thus affected; again, the mixed pentoxides used (61.4 Ta_2O_5 : 38.6 Nb_2O_5) behaved like niobic oxide. The probability of the occlusion of zirconia in HP was next investigated; four of the precipitates, taken at random, were analysed by Method B, Section XIII (ANALYST, 1928, 53, 518):

Exp.	Pentoxide taken. Grm.	Zirconia added. Grm.	HP . Grm.	ZrO_2 in HP . Grm.
15	Ta_2O_5 0.1017	0.0216	0.1040	0.0090
18	Ta_2O_5 0.1030	0.0520	0.0775	0.0112
23	Nb_2O_5 0.1028	0.0429	0.0984	0.0104
27	M_2O_5 0.1018	0.0732	0.1018	0.0206

These results leave no doubt in our mind that all the precipitates obtained must contain zirconia; hence the net earth-acid recovery errors are much larger than the apparent errors shown in the above Table. We conclude that zirconia creates a marked disturbance in the quantitative course of the reaction by inducing less complete earth-acid precipitation and by contaminating the hydrolysis precipitate.

E. THORIA (RARE EARTHS) AND EARTH ACIDS.—The very slight interference of thoria in tartaric hydrolysis, as compared to that of titania and zirconia, reflects the progressive change in chemical behaviour of the elements of Group IV. We conducted 8 tests with 1:1 mixtures of mixed pentoxides and thoria. It was observed in all cases that precipitation proceeded normally, but that a slight, permanent mistiness pervaded the solution after the precipitate had settled. The weighed *HP* was fused with bisulphate, the product dissolved in tartaric acid solution, and the unfiltered solution treated with oxalic acid. After several days' standing, the small precipitate was collected and weighed; being obviously impure, the precipitates from two tests were combined and re-treated, the thorium oxalate being re-precipitated from a very small bulk of filtered solution. For a confirmatory test, the purified thorium fractions were dissolved and tested with tannin in acetic solution, when they gave white (not orange) precipitates. Hence thoria is co-precipitated, but to a much smaller extent than titania and zirconia (see Exps. 43 to 46).

Two further tests (47 and 48) were made in exactly the same manner with a mixture of pentoxides and a preparation of ceria earths of unknown purity:

Exp.	M_2O_5 taken. Grm.	ThO_2 added. Grm.	Precipitant: 30 c.c. of	HP . Grm.	ThO_2 in HP :	
					Impure. Grm.	Purified.
43	0.0988	0.0980	HNO_3	0.1022	0.0049	0.0047
44	0.1008	0.1024	HCl	0.0978	0.0018	
45	0.1023	0.1024	HNO_3	0.1046	0.0010	0.0013
46	0.1032	0.1016	HCl	0.0976	0.0023	
		Ce_2O_3			Ce_2O_3 in HP :	
47	0.0974	0.100	HNO_3	0.0966	0.0009	doubtful
48	0.0954	0.100	HCl	0.0936	0.0014	

As far as the evidence goes, the rare earths do not appear to interfere in tartaric hydrolysis. When a supply of pure rare-earth preparations has been secured, it is intended to devote a special section to a study of the behaviour of the rare earths in the contemplated analytical scheme, and of their separation from the earth acids.

F. ALUMINA, BERYLLIA, FERRIC AND MANGANOUS OXIDES, AND EARTH ACIDS.—Alumina and beryllia could not be detected with certainty in *HP*, produced as described under E (Exps. 49 to 52). In Exps. 53 and 54, ferric oxide was traced in very small quantity in *HP* by means of sulphide precipitation from ammoniacal tartrate solution; it is quite likely, however, that part, at least, of this small amount was not present in the precipitate as weighed, but got introduced during the subsequent operations. Finally, the hydrolysis precipitates

obtained in presence of manganous oxide (Exps. 55 and 56) were tested by fusion with potassium carbonate and a little nitrate: no greenish tint, indicative of manganate, was observed.

Exp.	M_2O_3 taken.	Added. Grm.	Precipitant : 30 c.c. of	HP. Grm.	Purity of HP.		
	Grm.				Grm.		
49	0.1044	0.100 Al_2O_3	HNO_3	0.0988	0.0010 ¹	Al_2O_3 doubtful	
50	0.1048	0.100 do.	HCl	0.1020	0.0012 ¹		
51	0.1024	0.107 BeO	HNO_3	0.0986	0.0011 ¹	BeO doubtful	
52	0.1010	0.107 do.	HCl	0.0982	0.0010 ¹		
53	0.2008	0.050 Fe_2O_3	HNO_3	0.1956	0.0010	Fe_2O_3 do.	
54	0.2016	0.050 do.	HCl	0.1972	0.0006		
55	0.0982	0.100 MnO	HNO_3	0.0958	} MnO nil		
56	0.0974	0.100 do.	HCl	0.0952			

¹ Weight of small ammonia precipitate obtained in filtrate from hydrolysis of pyrosulphate melt.

CONCLUSIONS.—The great value of the tartaric hydrolysis reaction in qualitative analysis has been proved in Section XV (ANALYST, 1929, 54, 456). In the present paper, the quantitative course of the reaction has been elucidated.

(1) Towards nitric acid, tantalic, niobic, and tungstic acids react alike; their precipitation is complete but for a few mgrms., which remain dissolved as the result of what must be regarded as a balanced reaction.

(2) The separation of the earth acids from titania is far from perfect; but, used in conjunction with the oxalate and salicylate method (XIV, ANALYST, 1929, 54, 322), tartaric hydrolysis forms the first step of the most reliable separation procedure known to us.

(3) The presence of zirconia in substantial amounts is a complicating factor. The fact that tantalic, unaccompanied by niobic, acid is very incompletely precipitated when much zirconia is present is not to be regarded as a very serious matter, because the two earth acids almost invariably occur together; rather is it the contamination of the tartaric hydrolysis precipitate with zirconia that will have to be borne in mind when the method is applied. Fortunately the new pyrosulphate and tannin method (XV, *loc. cit.*) promises to become an effective and simple means for purifying the earth-acid precipitate from zirconia and titania; the question will be investigated at an early date.

(4) Thoria contaminates the hydrolysis precipitate to such a small extent that its complete removal, by any process achieving that of zirconia and titania, may be regarded as a foregone conclusion.

(5) Still less than thoria do the common metals and beryllium interfere. Iron can, in any case, be removed, previous to tartaric hydrolysis, by precipitation of ferrous sulphide from ammoniacal solution. The influence of the rare earths is yet to be studied.

(6) Nitric or hydrochloric acid may be used as the precipitant; in presence of oxalic acid, the earth-acid recovery is incomplete.

(7) The greatest weakness of the method lies in incomplete earth-acid precipitation (mentioned under 1), and this can be overcome, as will be shown in Section XVII below, by the application of one of two methods, neither of which necessitates the previous destruction of the tartaric acid.

SUMMARY.—Precipitation of the earth acids from tartrate solution by mineral acid, previously shown to be a sensitive and specific earth-acid reaction, has now been investigated as a quantitative method. Precipitation of tantalic and niobic, also tungstic, acids is never quite quantitative; a few mgrms. escape precipitation. Of all the other mineral associates of the earth acids, only titanium and zirconium interfere to a certain extent with the normal course of the reaction. Means for obviating this interference will be studied; the recovery of the small fraction of non-precipitated earth acid from the tartrate solution will be discussed in the next Section.

XVII. THE QUANTITATIVE PRECIPITATION OF THE EARTH ACIDS AND CERTAIN OTHER OXIDES FROM TARTRATE SOLUTION.

In the preceding Section, the quantitative course of the tartaric hydrolysis reaction has been investigated, it being shown, *inter alia*, that a few mgrms. of the earth acids escape precipitation. In this Section it will be proved that two reagents ensure quantitative recovery of the earth acids from tartrate solution, namely, tannin and cupferron. That being so, it may be asked why one of the reagents should not be applied at once to the quantitative precipitation of the earth acids without an intervening hydrolytic precipitation of the main fraction. Our answer is, that we favour tartaric hydrolysis, supplemented by tannin or cupferron precipitation, because the tartaric hydrolysis reaction, being more specific, permits of a more selective precipitation, yielding a main earth-acid fraction containing practically the whole of the tungstic acid, with other oxides, if any, as impurities. The next step—tannin or cupferron precipitation—furnishes the balance of the earth acids, together with other oxides that are quantitatively precipitated, but neither reagent precipitates the tartaric complex of tungsten. In view of the indefiniteness of the precipitation reactions of the more important constituents of earth-acid minerals, it is quite clear that their analysis is bound to include processes of fractional enrichment leading up to the final precipitation of the purified oxides. Another advantage of the procedure we advocate is this, that the tartaric hydrolysis precipitates are compact compared with the cupferron and, still more, with the bulky tannin precipitates. The latter are very suitable for micro-work.

A. TANNIN PRECIPITATION.

This new method is a practical application of an observation recorded in Section XI (ANALYST, 1928, 53, 265), namely, the precipitability of titania by tannin from neutralised tartrate solutions. In this paper the process is investigated at greater length, and extended to tantalum, niobium, zirconium, thorium, and aluminium.

EARTH ACIDS.—The quantitative precipitation of tantalum and niobium as tannin complexes from tartrate solutions presents no difficulties, as it takes place either in the neutralised solution or in moderately acid solution treated with alkali acetate. We proceed as follows: (1) The tartrate solution, containing 30 c.c. of hydrochloric acid (*i.e.* the filtrate from the tartaric hydrolysis) is titrated with ammonia (1:1), a bit of litmus paper in the liquid serving as indicator; the acid reaction is restored with a drop or two of dilute acid. The liquid is then boiled, and a fresh, strong solution of 0.5 grm. of tannin added; flocculation occurs after short boiling. (2) The same solution as in (1) is approximately neutralised with ammonia so as to remain slightly acid, boiled, and treated with excess of ammonium acetate and 0.5 grm. tannin, as before.

The precipitate from either procedure is collected, well washed with 2 per cent. ammonium chloride solution containing a little tannin, and ignited wet, finally at high temperature. The niobium precipitate is orange- to brownish-red, whilst the tantalum complex (which should be gale yellow) generally has a mauve hue, due to the presence of traces of iron.

RESULTS OF TEST ANALYSES.—The following remarks apply to all those tabulations below in which the weight of precipitate obtained (*P*) is given as "*gross*" and "*net*"; when the precipitation was quantitative, the result always gave a positive error, due to adsorption or, more probably, slightly incomplete washing out of alkali, and inclusion of a little silica and ferric oxide as unavoidable impurities. The weighed precipitates were therefore digested hot with acidulated water which was rendered ammoniacal, then filtered off, ignited, and again weighed; the precipitates were then fused with bisulphate, the product dissolved in tartaric acid, and the unfiltered solution made ammoniacal and treated with hydrogen sulphide. The small precipitate was collected, ignited, and weighed as ($\text{Fe}_2\text{O}_3 + \text{SiO}_2$), and its weight subtracted from that of the leached precipitate, the difference giving the "*net*" weight.

The following results were obtained by working with "unknown" quantities; in Exps. 1 to 5 the precipitation was done in the neutralised liquid, in 6 to 8 in slightly acid acetate solution:

Exp.	Taken M_2O_5 Grm.	<i>P</i> Gross. Grm.	<i>P</i> Net. Grm.	Error. Grm.	Exp.	Taken. Grm.	<i>P</i> Gross. Grm.	<i>P</i> Net. Grm.	Error. Grm.
Ta 1	0.0104	0.0107	0.0100	−0.0004	EA 9	ZrO_2 0.0257	0.0274	0.0255	−0.0002
Ta 2	0.0052	0.0061	0.0054	+0.0002	" 10	" 0.0257	0.0272	0.0255	−0.0002
Nb 3	0.0073	0.0084	0.0071	−0.0002	" 11	" 0.0263	0.0283	0.0265	+0.0002
EA 4	0.0038	0.0046	0.0033	−0.0005	" 12	" 0.0208	0.0234	0.0211	+0.0003
5	0.0068	0.0087	0.0072	+0.0004	" 13	TiO_2 0.0258	0.0280	0.0249	−0.0009
6	0.0178	0.0205	0.0175	−0.0003	" 14	" 0.0228	0.0242	0.0221	−0.0007
7	0.0054	0.0073	0.0052	−0.0002	" 15	ThO_2 0.0210	0.0227	0.0209	−0.0001
" 8	0.0102	0.0130	0.0099	−0.0003	" 16	" 0.0231	0.0246	0.0229	−0.0002
17	(0.0212 ZrO_2 + 0.0133 M_2O_5 + 0.0123 ThO_2)				=	0.0468	0.0492	0.0467	−0.0001
18	(0.0236 ZrO_2 + 0.0131 M_2O_5 + 0.0123 TiO_2)				=	0.0490	0.0518	0.0484	−0.0006

ZIRCONIA AND TITANIA.—When investigating the quantitative precipitation of zirconia by tannin, we at first obtained low and erratic results, which were

traced to incomplete precipitation even at low acid concentrations, as for titania (XI, *loc. cit.*). In oxalate solution the zirconium-tannin complex is likewise very sensitive to acid (XIII, ANALYST, 1928, 53, 516). In the course of further work we elaborated the following procedure, which not only secures a quantitative precipitation of zirconia, but answers equally well for the earth acids, titania, thorium, and mixtures of these oxides.

PROCEDURE.—The filtrate from the tartaric hydrolysis precipitate (acidity, 30 c.c. of hydrochloric acid) is treated with 1 gm. of tannin in strong solution, cooled, and carefully titrated with ammonia (1:1). A long strip of wet litmus paper is made to adhere to the side of the beaker so that the lower extremity is immersed in the liquid; in this manner the progress of neutralisation is easily observed in spite of the formation of a voluminous precipitate. The liquid is barely re-acidified, *i.e.* to the violet tint of the indicator, and boiled for two minutes. The neutralisation must be carried out with precision; if this is done, the precipitation is quantitative, even though no acetate is added; but we include treatment of the solution with 5 grms. of ammonium acetate at this point, so as to provide for the possible formation of soluble complex beryllium acetate (*cf.* Moser and Niessner, ANALYST, 1928, 53, 403). The precipitate is left to settle, collected, and treated and purified exactly as the earth-acid precipitates in Exps. 1 to 8. The results (Exps. 9 to 14) show that quantitative precipitation is achieved by the above procedure, the distinctive feature of which is addition of tannin before neutralisation. An excess of ammonia must be avoided, as it would lead to co-precipitation of divalent metals (*e.g.* beryllium, manganese); double precipitation may be required in the analysis of minerals.

THORIA; MIXED OXIDES.—The precautions required for the quantitative precipitation of zirconia can, apparently, be relaxed in the case of thorium, as this oxide is precipitated by tannin from approximately neutralised, boiling tartrate solutions on addition of ammonium acetate, as in the case of the earth acids; however, we used the procedure just described under zirconia, as it should be applied systematically to all unknown mixtures. The results for thorium and two ternary oxide mixtures are tabulated as Exps. 15 to 18.

ALUMINA.—The co-precipitation of the minute quantities of iron accidentally present in the above tests led us to infer that alumina also might be precipitated from tartrate solutions by the tannin reaction. Such is actually the case, alumina being quantitatively recovered by partial neutralisation and boiling with ammonium acetate and tannin, as described under Earth Acids; it is unnecessary to neutralise as closely as for zirconia.

This observation seems to us of analytical importance beyond the special subject of earth-acid analysis. The separation of small quantities of alumina from much iron is quite frequently required in ore analysis. Precipitation of the alumina by thiosulphate, or its conversion into soluble alkali aluminate, are processes of questionable value. Determination by difference, after volumetric determination of the iron in the weighed mixed oxides, is wrong in principle,

because the subordinate constituent should actually be determined. Precipitation of ferrous sulphide from ammoniacal tartrate solution is an accurate separation process, but the determination of the alumina in the filtrate by the usual methods necessitates destruction of the tartaric acid. Now the tannin method renders that manipulation unnecessary; after precipitating the iron as sulphide, we dilute the ammoniacal tartrate solution to a definite volume, and filter an aliquot portion. This saves time, as the washing of bulky ferrous sulphide precipitates is tedious; and, even if the amount of alumina is very small, part of the solution suffices, because the aluminium-tannin complex is exceedingly bulky; hence it is well suited for micro-work, but inconveniently large for more than 0.02 grm. of Al_2O_3 .

The ammoniacal tartrate filtrate is acidified with acetic acid, and boiled till hydrogen sulphide is expelled; 5 to 10 grms. of ammonium acetate chloride, if not already present, and a fresh solution of tannin (1 grm.) are then added, and boiling is continued for a few minutes. After settling, the buff-coloured precipitate is collected, washed with dilute ammonium nitrate solution containing a little tannin, ignited wet, and weighed. If more than a few mgrms., it should be digested with hot water and a drop of nitric acid, which is neutralised by ammonia before filtration; the precipitate is again collected, washed, ignited strongly, and weighed as Al_2O_3 . Four test separations of "unknown" mixtures gave the following results:

Exp.	Fe_2O_3 .			Al_2O_3 .		
	Taken.	Found.	Error.	Taken.	Found.	Error.
	Grm.	Grm.	Grm.	Grm.	Grm.	Grm.
19	0.1131	0.1140	+0.0009	0.0066	0.0074	+0.0008
20	0.0954	0.0956	+0.0002	0.0114	0.0116	+0.0002
21	0.0764	0.0768	+0.0004	0.0079	0.0081	+0.0002
22	0.1108	0.1103	-0.0005	0.0024	0.0025	+0.0001

REACTION FOR ALUMINIUM.—We have discovered another reaction of aluminium not described in the literature. Aluminium solutions containing free tartaric acid are not precipitated by phosphate in the cold, but boiling causes precipitation (zirconium gives the same reaction: *I, J. Chem. Soc.*, 1921, 120, 1931); an ammoniacal tartrate solution, on the other hand, is not precipitated, ammonia re-dissolving the precipitate obtained in the hot acid liquid. When alumina is precipitated by tannin from tartrate solutions containing phosphate, the precipitate is free from phosphate.

Gallium reacts like aluminium, being precipitated by tannin from tartrate solution (Moser and Brukl, *Monatsh. Chem.*, 1929, 51, 79).

B. CUPFERRON PRECIPITATION.

Cupferron precipitation of the earth acids has been studied by Pied (ANALYST, 1925, 50, 36), who finds that they are recovered quantitatively from solutions containing oxalic, tartaric, and sulphuric acid. The reagent is added to the cold solution during vigorous agitation; the precipitate is filtered off at once, washed with dilute sulphuric acid, and ignited gradually. Titania also is precipitated.

PRECIPITATION FROM TARTRATE SOLUTION.—We desired to do some further tests on cupferron precipitation from tartrate solution so as to be able to apply the procedure, if necessary, to the recovery of the small quantities of earth acid not precipitated in the tartaric hydrolysis. In this investigation we were fortunate to have the co-operation of Messrs. G. E. F. Lundell and H. B. Knowles, of the U.S. Bureau of Standards, who have made a special study of cupferron precipitation methods (ANALYST, 1920, 45, 237). Dr. Lundell kindly gave us the following account of the work: The oxide was fused with potassium carbonate, and the melt dissolved in sulphuric and tartaric acids. A preliminary precipitation with cupferron was made, and the precipitate ignited and weighed. The object of this operation was, to remove any possible impurities not precipitated by cupferron. The weighed precipitate, P^1 , was brought into solution (200 c.c.) as before, and the cupferron precipitation repeated at acid concentrations given below. A large excess of cupferron (50 c.c. of 6 per cent. solution) and addition of macerated paper were thought advisable, and the solutions cooled in ice-water for 30 minutes before filtration; the precipitates, P^2 , were washed with 10 per cent. hydrochloric acid containing a little cupferron, and ignited:

Exp.	P^1 Grm.	P^2 Grm.	Error. Grm.	Acidity per cent.	
				$C_4H_4O_6$	H_2SO_4
1	0.1936 Nb_2O_5	0.1930	-0.0006	5	5
2	0.1947 "	0.1942	-0.0005	5	10
3	0.1962 Ta_2O_5	0.1961	-0.0001	5	5
4	0.1955 "	0.1946	-0.0009	5	10

The results show a very slight negative error, though no earth acid could be detected in the filtrates. Messrs. Lundell and Knowles are of the opinion that the precipitation may be regarded as complete within the limits of experimental error. They find the niobium precipitate to be bulkier than that of tantalum, and to coagulate more readily; we confirm this observation.

Our own tests were conducted with small, "unknown" amounts of pentoxides in solutions (250 to 300 c.c.) containing 30 c.c. of strong hydrochloric acid partly neutralised with 10 c.c. of strong ammonia, in view of a possible future application under these conditions. The bisulphate melt was brought into solution with 3 grms. of tartaric acid; the liquid, after addition of acid and ammonia, was left to cool, and treated during agitation with a filtered cupferron solution; nearly one gram. of reagent proved to be required for satisfactory flocculation. The precipitates were filtered off after less than an hour, washed with 10 per cent. hydrochloric acid, ignited, and weighed. Positive errors were recorded, due to contamination with ferric oxide and silica, as before; these impurities were determined and deducted, the difference giving the "net" weight:

Exp.	Taken. Grm.	P Gross. Grm.	P Net. Grm.	Error. Grm.
23	Ta_2O_5 0.0210	0.0224	0.0210	0.0000
24	" 0.0283	0.0296	0.0278	-0.0005
25	Nb_2O_5 0.0251	0.0260	0.0249	-0.0002
26	" 0.0285	0.0298	0.0285	0.0000
27	ZrO_2 0.0257	0.0260	—	+0.0003

Two further tests were made along the same lines with 0.02 grm. portions of tungstic oxide: no precipitation took place.

The earth-acid recovery is satisfactory, with a slight tendency towards a negative error. From the practical point of view we are inclined to favour precipitation with tannin, this being the more easily procurable and stabler reagent; the precipitates produced by it flocculate much more readily; hence for very small quantities of pentoxides the tannin method appears more reliable. Alumina is precipitated by tannin, but not by cupferron under these conditions. As regards the rare earths, Lundell and Knowles (*loc. cit.*) state that cerium is not without influence on the cupferron precipitation of titanium and zirconium. The action of tannin on tartrate solutions of the rare earths will be investigated.

C. ANALYTICAL APPLICATION.

Precipitation of small quantities of earth acid from tartrate solution by tannin or cupferron supplements tartaric hydrolysis; a combination of the two processes enables us to precipitate large or small amounts quantitatively without having to destroy the tartaric acid. In Exps. 28 and 29, the tartrate solution was hydrolysed with 30 c.c. of hydrochloric acid, which gave *HP*; the filtrate was precipitated with tannin after approximate neutralisation and addition of ammonium acetate, yielding *TP*:

Exp.	Taken. Grm.	<i>HP</i> . Grm.	<i>TP</i> . Grm.	<i>ΣP</i> . Grm.	Error. Grm.
28	Ta ₂ O ₅ 0.1065	0.1052	0.0013	0.1065	0.0000
29	Nb ₂ O ₅ 0.1014	0.0927	0.0084	0.1011	-0.0003

PRECIPITATION REACTIONS FOR EARTH-ACID MINERALS.—We now dispose of a number of precipitation reactions from tartrate solution capable of being applied to the analysis of earth-acid minerals, namely: (1) Hydrogen sulphide in acid tartrate solution precipitates tin, antimony, etc. (2) Tantalum, niobium (major fraction), and tungsten are precipitated by tartaric hydrolysis. (3) The sulphides of iron and uranium (manganese partly) are precipitated from ammoniacal solution. (4) Oxalic acid precipitates thorium and the rare earths from acid solution (Pied, *loc. cit.*). (5) Cupferron precipitates the earth acids (minor fraction), titania, and zirconia. (6) The oxides enumerated under (5) are precipitated by tannin from the neutralised solution, together with thorium and alumina. (7) The metals still left in the tartrate solution are manganese (major fraction), beryllium, calcium, and magnesium; they are recovered after the destruction of the organic compounds, though this may not prove obligatory: beryllium and manganese give a tannin, calcium an oxalate, magnesium a phosphate, precipitate in ammoniacal solution. The order in which some of the above reactions will be applied, and other details of procedure, remain to be investigated.

SUMMARY.—The earth acids are quantitatively precipitated from tartrate solution by tannin after neutralisation or addition of excess of ammonium acetate; we utilise this reaction for the recovery of the earth acid fraction not precipitated

by tartaric hydrolysis. Zirconia and titania are likewise precipitated, but accurate neutralisation after addition of the tannin is required. Thoria and alumina are precipitated like the earth acids. The reaction is useful and convenient for the direct determination of small quantities of alumina after precipitation of iron as sulphide. Cupferron is available for the quantitative recovery of the earth acids from tartrate solutions in presence of mineral acid. The earth acids and their mineral associates are classed into analytical groups according to their precipitability from tartrate solution.

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A Study of the Methods of Determining Boron Compounds in Food and Drugs.

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(Work done under the Analytical Investigation Scheme.)

PART II. EXPERIMENTAL: EFFECT OF FATS AND OTHER ORGANIC SUBSTANCES ON THE DETERMINATION.

PRACTICAL experience has shown that substances containing large percentages of fat cannot be ignited, even in presence of excess of alkali, without considerable loss of boron compounds resulting. Special methods, such as that of Richmond and Harrison (ANALYST, 1902, 27, 179) have been devised to get over the difficulty, but their application is limited to substances like butter, margarine, or egg melanges, which can readily be transformed into a homogeneous fluid condition. Substances such as ham, sausages, cakes and fruits, however, apparently cause considerable difficulty, as none of these can be rendered homogeneous by means of ordinary solvents. Since the presence of fat or oil is the chief source of trouble, the following series of experiments was tried with a view to discovering if, under any condition, the fat can readily be removed without any loss of boric acid.

SOLUBILITY OF BORIC ACID IN ORGANIC SOLVENTS AT 60° F.—Weighed quantities of pure dry boric acid were stirred for 5 minutes in a dry beaker with 20 c.c. of methylated ether, petroleum spirit, benzene, chloroform and carbon tetrachloride, respectively, the temperature being maintained at 60° F. In a second series of experiments 5 c.c. of pure olive oil were added in each case. The contents of the beaker were then filtered through a Swedish filter paper into a dry beaker, and 10 c.c. of each filtrate were evaporated to dryness in a porcelain basin (care being taken to keep the solvent below its boiling point during the evaporation), the residue was taken up with 10 to 15 c.c. of distilled water, and

the solution titrated after the addition of 0.5 gm. of mannitol and phenolphthalein. (In each case the solution was tested and found to be neutral before the mannitol was added.)

The remaining portion of the filtrates was tested qualitatively with turmeric paper for the presence of boric acid.

In the case of the filtrates containing oil, 10 c.c. were extracted with 5 c.c. of 0.5 *N* sodium hydroxide solution and about 30 c.c. of water. The extracts (about 50 c.c. in volume) were acidified, boiled for 5 minutes, cooled, neutralised with sodium hydroxide solution (with Sofnol Indicator No. 1), and finally titrated after the addition of 0.5 gm. of mannitol and six drops of phenolphthalein solution.

TABLE I.

Solvent 20 c.c.	Quantity of boric acid taken. Grms.	Final titration.		Reaction.
		0.1 <i>N</i> NaOH c.c.	$\approx \text{H}_3\text{BO}_3$ (actual). Grm.	
Ether (dry)	0.051	0.64	0.0040	Very distinct
" " " " " " " "	0.052	0.40	0.0025	" "
Petroleum spirit	0.051	<0.01	—	Practically nil
Chloroform	0.052	0.01	0.0006	Distinct trace
Benzene	0.049	<0.01	—	Practically nil
Benzene+ trace of alcohol ..	0.050	0.01	—	Distinct trace
Carbon tetrachloride	0.051	<0.01	—	Practically nil
15 c.c. ether+ 5 c.c. oil	0.052	0.75	0.0047	Very distinct
15 c.c. ether+ 5 c.c. oil	0.051	1.00	0.0062	" "
Petroleum spirit+ 5 c.c. oil ..	0.053	<0.01	—	Practically nil
Chloroform+ 5 c.c. oil	0.050	0.07	0.0043	Very distinct
Benzene+ 5 c.c. oil	0.052	<0.01	—	Practically nil
Carbon tetrachloride+ 5 c.c. oil	0.051	0.28	0.0017	Very distinct

The above results show that solvents, such as petroleum spirit, benzene and carbon tetrachloride, which do not readily mix with water, dissolve practically no boric acid. Ether and chloroform, on the other hand, dissolve a small quantity at 60° F. In the above experiments the solubility, except with ether, was found to be less than 1 part in 10,000 of solvent, but the proportion in all cases probably depends upon the amount of moisture the solvent has taken up during the course of the test. The presence of a minute trace of alcohol mixed with benzene was found to render boric acid more soluble than in the pure dry benzene.

The solubility of boric acid in mixtures of oil and benzene or petroleum spirit at 60° F. is practically negligible. Mixtures of pure olive oil and methylated ether, chloroform or carbon tetrachloride, on the other hand, dissolve small, but quite appreciable, quantities of boric acid. It is, however, quite possible that different oils and fats might behave differently from olive oil, but this may readily be verified by subsequent tests.

In view of the fact that some products are more or less acid, and that some of their boric acid content may be lost if they are dried without previous neutralising with caustic soda, another series of experiments was tried, in which about 0.5 gm. of boric acid and 10 c.c. of *N* sodium hydroxide solution were evaporated to dryness before stirring up with the solvents. The results are shown below:

TABLE II.

SOLUBILITY OF SODIUM BORATE IN ORGANIC SOLVENTS AT 60° F.

Oil or fat.	Solvent.	Boric acid reaction of filtrate.
Olive oil	Ether	Distinct
"	Petroleum spirit	Practically nil
"	Benzene	Practically nil
"	Chloroform	Distinct
"	Carbon tetrachloride	Distinct trace
Cocoa butter	Ether	Distinct
"	Petroleum spirit	Practically nil
"	Benzene	Practically nil
"	Chloroform	Distinct
"	Carbon tetrachloride	Distinct trace

As shown by the foregoing experimental results, benzene and petroleum spirit can be used to eliminate fats and oils from vegetable products by merely washing out at room temperature and rejecting. The quantity of boric acid dissolved thereby is practically negligible if the product is first dried, either alone or after being rendered slightly alkaline with caustic soda. This has an important practical bearing, as much time might thus be saved. Perfect dryness, however, is essential, and it is safer to determine the quantity of boric acid in the extract as shown below.

The following experiment was tried to ascertain whether, instead of rejecting the filtrate containing the excess of fat, the quantity of boric acid could be directly titrated and allowed for:

TABLE III.

Fat or oil.	Solvent.	Boric acid added. Grm.	Titration.	
			0.1 N NaOH c.c.	= H ₃ BO ₃ . Grm.
Olive oil	Ether	0.0195	3.14	0.0195
" "	Petroleum spirit	0.0195	3.14	0.0195
" "	Benzene	0.0195	3.14	0.0195
" "	Chloroform	0.0195	3.14	0.0195
" "	Carbon tetrachloride	0.0195	3.14	0.0195

As shown in Table III, the presence of oil, together with methylated ether, petroleum spirit, benzene, chloroform or carbon tetrachloride, does not affect the accuracy with which boric acid solutions can be titrated. In these experiments a known quantity (3 c.c.) of boric acid solution was titrated direct, with the use of 0.5 gm. of mannitol and phenolphthalein. Similar quantities were placed in a porcelain basin, together with 5 c.c. of olive oil and 15 c.c. of the above organic solvents, in turn. About 30 c.c. of water were added, and the contents of the basin were heated for 5 minutes on a water-bath, with constant stirring, and then cooled. The contents were then titrated with 0.1 N sodium hydroxide solution, after the addition of 0.5 gm. of mannitol and phenolphthalein, and the results were recorded as shown in the Table.

These results are of importance in so far as they show how the usual lengthy determination of boric acid in products containing a large percentage of fat may be

shortened considerably. Now that it is known that the determination of boric acid may be made direct on the fat-solvent portion without first extracting with alkali, the product under examination can be dried, washed with a solvent into a titrating basin, and the extracted boric acid determined and added to the result obtained in the main determination.

One would, however, require to select a solvent and carry out the extraction of the oil or fat under such conditions as would prevent the extraction of any phosphates along with the boric acid. A further investigation would, therefore, require to be made to ascertain under what conditions the phosphates would be excluded.

EFFECT OF CONCENTRATION OF FAT ON LOSS OF BORIC ACID WHEN IGNITED WITH EXCESS OF ALKALI.—Three different quantities of boric acid solution containing 0.0124 gm., 0.0186 gm., and 0.0310 gm. of boric acid, respectively, were placed in a platinum basin together with 3 c.c. of *N*-sodium hydroxide solution. The contents of the basin were evaporated to dryness on a water-bath, and different weights of olive oil were added. The oil, borate and excess of alkali were then heated gradually, ignited and burned off at a dull red temperature. The ash was boiled with water containing a slight excess of *N*-sulphuric acid, filtered, and washed into a flat titrating basin. The contents of the basin were boiled for 5 minutes to ensure the complete expulsion of carbonic anhydride and then cooled. One drop of Sofnol Indicator No. 1 was added, and 0.1 *N* sodium hydroxide solution was carefully run in from a burette until the liquid was just neutral. The burette was now filled up and carefully adjusted for the final titration of the boric acid. Then 0.1 gm. of mannitol and about 6 to 8 drops of phenolphthalein solution were added, and the contents were titrated.

In order to determine more accurately the loss due to the oil the following experiment was tried:—Three platinum basins, each containing 0.0186 gm. of boric acid and 3 c.c. of *N*-sodium hydroxide solution, were heated on a water-bath until complete evaporation of the contents had taken place. Two were then heated alone, one at a dull red heat, and the other at a high temperature. The former was found to contain 0.0183 gm. of boric acid, and the latter 0.0174 gm. That is, the ignition of 0.0186 gm. of boric acid in the presence of excess of alkali caused a loss of 0.0003 gm. of boric acid at a dull red heat, and of 0.0012 gm. of boric acid at a high temperature.

The contents of the third platinum basin were ignited with 10 gm. of stearic acid and treated as in the experiments with the olive oil. The ash, when finally titrated, was found to contain 0.0178 gm. of boric acid.

This experiment showed that if one took into account the difficulty of igniting a highly carbonaceous substance like stearic acid, the loss due to the presence of the stearic acid was very similar to that of the borate when ignited alone. In other words, the presence of a fatty acid causes little loss of boric acid when ignited with excess of alkali.

The following table shows the losses of boric acid which occurred on igniting olive oil with borate and excess of alkali:

TABLE IV.

EFFECT OF CONCENTRATION OF FAT ON LOSS OF BORIC ACID WHEN
IGNITED WITH EXCESS OF ALKALI.

Quantity of fat taken.	Quantity of boric acid added.		Final titration.	
	Grms.	Percentage in fat.	0.1 N NaOH c.c.	=H ₃ BO ₃ Grm.
1	0.0124	1.24	1.60	0.0099
1	0.0186	1.86	2.22	0.0138
1	0.0310	3.10	4.42	0.0274
5	0.0124	0.248	0.63	0.0039
5	0.0186	0.372	0.94	0.0058
5	0.0310	0.620	1.50	0.0093
10	0.0124	0.124	0.45	0.0028
10	0.0186	0.186	0.72	0.0045
10	0.0310	0.310	1.40	0.0087
15	0.0124	0.083	0.65	0.0040
15	0.0186	0.124	0.63	0.0039
15	0.0310	0.207	0.68	0.0042
20	0.0124	0.062	1.30	0.0081
20	0.0186	0.093	0.50	0.0031
20	0.0186	0.093	0.75	0.0046
20	0.0310	0.155	1.40	0.0087

In each test 3 c.c. of N sodium hydroxide were used for fixing the boric acid during ignition.

These results show that when 1 gram. of oil was used the loss, though considerable, was distinctly irregular. Greater regularity was observed when 5 grms. and upwards of oil were used. This is shown by the following tabulated results, which were calculated from the figures found in Table IV.:

TABLE V.

H ₃ BO ₃ present. Per Cent.	H ₃ BO ₃ found. Per Cent.	H ₃ BO ₃ lost. Per Cent.	Percentage of total H ₃ BO ₃ lost.
0.062	0.016	0.046	74.2
0.083	0.026	0.057	69.4
0.083	0.027	0.056	68.7
0.093	0.023	0.070	75.3
0.124	0.028	0.096	77.4
0.124	0.028	0.096	77.4
0.155	0.044	0.111	71.6
0.186	0.045	0.141	75.7
0.207	0.054	0.153	73.9
0.248	0.085	0.163	69.4
0.310	0.087	0.223	71.9
0.372	0.116	0.256	68.8
0.620	0.186	0.434	70.0

It will be observed that the percentage of boric acid lost under the above conditions is very large, and, although not very constant, yet possesses a degree of constancy which suggests that if the conditions of ignition were more uniform a fairly constant percentage loss would result.

The losses shown in Table V fluctuate between 68.7 and 77.4 per cent., and have a mean value of 72.6 per cent.

In view of the fact that a very small percentage only of boric acid is lost when ignited, either with alkali alone or with alkali and a fatty acid, it is evident that

the loss must be due to the glyceride present when an oil is used. The apparent constancy of loss appears to suggest that, when excess of oil and caustic alkali is present, a complex consisting of a sodium salt, borate and glycerol is formed in course of ignition, and that this complex splits up into sodium borate and glyceroborate. This contains about 70 per cent. of the original borate, and is volatilised in the course of ignition, leaving sodium borate.

In order to ascertain whether the amount of alkali in excess of that required to neutralise the boric acid was an important factor, different quantities of caustic soda were added to the same quantities of boric acid and olive oil prior to ignition. It was found, however, that the results obtained were so similar as to admit of the conclusion being drawn that, so long as the sodium hydroxide was in excess, the amount was immaterial.

It is also quite evident from the above experiments that, so long as there is sufficient oil or fat present to provide the necessary glycerol for the boric acid present, the quantity of oil or fat is also immaterial.

VARIATION IN THE LOSS OF BORIC ACID CAUSED BY IGNITING DIFFERENT OILS IN PRESENCE OF BORIC ACID AND EXCESS OF ALKALI.—Similar weights (5 grms.) of different fats and oils were ignited with known weights of boric acid and excess of sodium hydroxide at a dull red heat. The ash was digested with water and 6 drops of concentrated hydrochloric acid, and filtered into a titrating basin. The filter paper and contents were returned to the platinum basin and fully ignited, and then washed into the basin. The contents of the basin were boiled for 5 minutes, with constant stirring, to expel the carbonic anhydride, cooled, neutralised, and then titrated after the addition of 0.5 gram. of mannitol. The results obtained are given in the following Table:

TABLE VI.

Kind of oil 5 grms.	N-NaOH added. c.c.	Loss of H_3BO_3 . Per Cent.	Boric acid H_3BO_3 added. Grm.	Final titration.	
				0.1 N NaOH. c.c.	= H_3BO_3 . Grm.
Coconut butter	3.0	73.0	0.0189	0.83	0.0051
" " "	3.0	73.5	0.0189	0.81	0.0050
Olive oil	3.0	69.0	0.0186	0.94	0.0058
" " "	3.0	70.0	0.0186	0.90	0.0056
Almond oil	3.0	58.6	0.0189	1.25	0.0078
" " "	3.0	58.2	0.0189	1.28	0.0079
Cacao butter	3.0	61.4	0.0189	1.18	0.0073
" " "	3.0	60.3	0.0189	1.21	0.0075
Linseed oil	3.0	56.4	0.0186	1.30	0.0081
" " "	3.0	46.4	0.0186	1.30	0.0081
Castor oil	3.0	56.1	0.0189	1.34	0.0083
" " "	3.0	54.5	0.0189	1.38	0.0086
Sesame oil	3.0	54.0	0.0199	1.40	0.0087
" " "	3.0	54.5	0.0189	1.38	0.0086
Rape oil	3.0	50.8	0.0189	1.50	0.0093
" " "	3.0	50.3	0.0189	1.51	0.0094
Cottonseed oil	3.0	49.2	0.0186	1.65	0.0102
" " "	3.0	44.0	0.0186	1.70	0.0105
" " "	3.0	51.1	0.0186	1.47	0.0091

From these results it will be observed that different kinds of fat or oil give rise to variations in the percentage of boric acid volatilised and lost during the process of ignition. The proportion of loss is fairly constant for the same kind of oil, and appears to have some bearing on the constitution of the oil. As already mentioned, the glycerol content of an oil plays an important part in rendering boric acid volatile, so that there appears to be some possibility of utilising the ignition of boric acid in presence of excess of alkali as a means of identifying a glyceride (fat or oil), and also of determining the amount of glycerol contained in compounds or mixtures. The above results were obtained under ordinary laboratory conditions, but, so far as they go, they afford reason for the belief that, if special precautions were taken, which would keep the conditions constant and exclude any disturbing factors, characteristic results would be found for individual oils and fats.

EFFECT OF THE PRESENCE OF ORGANIC MATTER ON THE LOSS OF BORIC ACID WHEN IGNITED WITH EXCESS OF ALKALI.—Twenty grms. each of different organic substances which were free from boric acid, were ignited at a dull red heat in a platinum basin with a known quantity of boric acid and excess of alkali (3 c.c. of 0.1 N H_3BO_3 + 3 c.c. of N -NaOH). The boric acid was then determined in the usual way after lixiviating and eliminating carbonic anhydride and phosphates, if present. When the substance (*e.g.* sugar) contained no phosphates, the ash was boiled with water and a slight excess of hydrochloric acid until most of the carbonic anhydride was expelled, and the solution was then transferred to a 100 c.c. flask, made up to the mark, shaken and filtered. Fifty c.c. of the filtrate were placed in a porcelain titrating basin and boiled for 5 minutes, with constant stirring, to ensure the complete expulsion of carbonic anhydride. After rapid cooling, the contents were neutralised with 0.1 N sodium hydroxide solution, Sofnol Indicator No. 1 being used. The final titration was effected after adding 0.5 gm. of mannitol and phenolphthalein solution. For convenience, these results are shown in the following Table doubled to equal the entire quantity.

The starch was found to contain a small percentage of phosphates, which rendered the above shortened method inapplicable. The boric acid in the ashes obtained from mixtures containing starch was therefore determined by the usual long method.

The following Table, No. VII (see p. 722), shows the results obtained.

These results indicate that substances of the nature of carbohydrates and fatty acids do not have any considerable effect on the loss of boric acid, when ignited in presence of excess of alkali. It will be observed that a slight loss does take place, but it is insignificant when compared with that produced by the ignition of an oil or fat, and is, in reality, not much more than is caused by the ignition of boric acid and excess of alkali alone. There are certainly slight differences with different substances, but these appear to be mainly due to the variation in the inflammability of these substances. The loss of boric acid in these cases would therefore be mechanical rather than chemical, as in the case of substances containing glycerol.

TABLE VII.

EFFECT OF THE PRESENCE OF ORGANIC MATTER ON THE LOSS OF BORIC ACID WHEN
IGNITED WITH EXCESS OF ALKALI.

				Boric acid taken.		Final titration.	
Substance, 20 Grms.				Grm.	Percentage of substance.	0.1 N NaOH.	=H ₃ BO ₃
						c.c.	Grm.
Olive oil	0.0186	0.093	0.76	0.0047
Sugar	0.0186	0.093	2.98	0.0185
Starch	0.0186	0.093	2.96	0.0184
Stearic acid	0.0186	0.093	2.84	0.0176
19 sugar and 1 oil	0.0186	0.093	2.96	0.0184
18 sugar and 2 oil	0.0186	0.093	2.40	0.0149
15 sugar and 5 oil	0.0186	0.093	{ 1.68 1.80	0.0104 0.0112
19 starch and 1 oil	0.0186	0.093		2.90
18 starch and 2 oil	0.0186	0.093	{ 2.38 2.46	0.0148 0.0153
15 starch and 5 oil	0.0186	0.093		2.38
19 starch and sugar and 1 oil	0.0186	0.093	2.94	0.0182
18.8 starch and sugar and 1.2 oil	0.0186	0.093	2.78	0.0172
18.6 starch and sugar and 1.4 oil	0.0186	0.093	2.30	0.0143
18.4 starch and sugar and 1.6 oil	0.0186	0.093	2.00	0.0124
18.2 starch and sugar and 1.8 oil	0.0186	0.093	2.04	0.0126
18 starch and sugar and 2 oil	0.0186	0.093	1.88	0.0117

A comparison of the results shown in Table VII with those in Table IV shows that the presence of carbohydrates with fat tends to diminish the loss of boric acid which would have been caused by the presence of the same amount of fat by itself. Thus, for example, 1 gram. of olive oil ignited with 0.0186 gram. of boric acid and 3 c.c. of *N* sodium hydroxide causes an actual loss of 0.0048 gram. of boric acid, whilst 1 gram. of olive oil, together with 19 grms. of sugar, ignited with 0.0186 gram. of boric acid and 3 c.c. of *N* sodium hydroxide solution causes an actual loss of merely 0.0002 gram. of boric acid. Also, 5 grms. of olive oil under the above conditions causes an actual loss of 0.0128 gram. of boric acid, whereas 5 grms. of olive oil and 15 grms. of sugar causes a loss of 0.0069 gram. of boric acid; and 5 grms. of olive oil and 15 grms. of starch causes a loss of only 0.004 gram. of boric acid. The difference in these last two results is probably due to the dry nature of the starch affording a better protecting medium between the oil and the sodium borate than sugar, as a mixture of oil and sugar allows a quantity of the oil to come into direct contact with the sodium borate, thereby causing greater loss when the mass is ignited. In some instances the experiments were repeated several times before concordant results were obtained. This difficulty appeared to be caused by the variations in the degree of contact between the oil and the sodium borate.

The conditions of the foregoing experiments are to a large extent artificial, and the oil and the boric acid are by no means as homogeneously mixed with the starch, etc., as they would be in natural vegetable substances. The protective properties of the non-fatty constituents would, therefore, tend to be more variable. So far as the above results go, it would appear that comparatively little loss of boric acid occurred during direct ignition if the percentage of oil or fat in the

sample did not exceed 5 per cent. If that were absolutely correct for all substances, then Thomson's process could be curtailed by directly igniting in presence of excess of alkali any substance which was known to contain less than 5 per cent. of oil.

The following table shows some results obtained by the use of natural vegetable substances in place of artificial mixtures of starch, sugar and oil:

TABLE VIII.

EFFECT OF THE PERCENTAGE OF FAT OR OIL IN VEGETABLE PRODUCTS ON THE LOSS OF BORIC ACID ON IGNITION.

Article, 20 grms.	Containing in 20 grms.		Boric acid added. Grm.	Final Titration.	
	H_3BO_3 .	Oil.		For	$\equiv H_3BO_3$.
	Grm.	Grm.		$\frac{1}{2}$ quantity. c.c.	Grm.
Dairy meal ..	0.0001	1.30	0.0188	1.45	0.0090
" " "	0.0001	1.30	0.0310	2.43	0.0151
Soya meal ..	0.0005	0.14	0.0188	1.46	0.0091
" " "	0.0005	0.14	0.0310	2.41	0.0149
Dried grains ..	Nil	1.43	0.0188	1.48	0.0092
" " "	—	1.43	0.0310	2.43	0.0151
Kardi seed cake	0.0003	1.73	0.0189	1.48	0.0092
" " "	0.0003	1.73	0.0313	2.48	0.0154
Calf meal ..	0.0003	1.69	0.0310	2.45	0.0152

The loss of boric acid is shown in the following table:

TABLE VIIIa.

Loss of boric acid H_3BO_3 .

Article, 20 grms.	Oil. Per Cent.	Percentage of total boric acid.	
		Grm.	
Dairy meal ..	6.50	0.0009	4.75
" " "	6.50	0.0009	2.90
Soya meal ..	0.70	0.0011	5.70
" " "	0.70	0.0017	5.08
Dried grains ..	7.15	0.0004	2.13
" " "	7.15	0.0008	2.58
Kardi seed cake ..	8.65	0.0008	4.16
" " "	8.65	0.0008	2.53
Calf meal " ..	8.45	0.0009	2.88

From the above results it will be observed that a slight loss of boric acid has taken place in each determination. It is apparent, however, that the loss bears no relationship to the percentage of oil or fat present in the sample, and is, in fact, greater in the case of the extracted soya meal, which contained little oil, than in any of the other samples. The comparatively low results with this sample may be attributed to losses other than those caused by ignition, as the large percentage of phosphates and other mineral matter rendered the separation of the boric acid extremely difficult. The other actual quantities of boric acid lost are more constant, and are comparable with the loss due to the ignition of fat-free organic matter and boric acid together with excess of alkali. It would appear, therefore, that there is a tendency towards slightly low results. The deficiency may amount to about 0.0008 grm. of boric acid (H_3BO_3), but should be considerably less in the case of substances which do not contain high percentages of phosphates and other mineral constituents.

As already mentioned, the loss of boric acid, due to the oil in a sample, depends upon the degree of contact between the oil and the boric acid. The samples used in this experiment did not appear oily, and, apparently, the contact of the oil and the boric acid is very slight, as even 8.65 per cent. of oil causes no definite loss. In all probability the percentage of oil in some natural vegetable products could be increased still further without causing any appreciable loss of boric acid. As, however, the constitution of some vegetable products may give rise to greater contact between the oil and boric acid present, it would be inadvisable to take too high a percentage of oil as the general margin of safety.

Taking everything into consideration, it would appear that any vegetable substances which contains less than 8 per cent. of oil, may be safely ignited directly without previous extraction of the oil, and that no appreciable loss of boric acid will result therefrom.

By taking 8 per cent. of oil as a general margin of safety, and omitting the preliminary extraction of oil in all samples containing 8 per cent. of oil and under, considerable time and trouble will be saved. It is, however, imperative to mix such samples with a solution of alkali, and to dry them thoroughly at water-bath temperature before attempting to ignite them, as the presence of moisture causes a loss of boric acid if an attempt is made to ignite a moist sample.

LOSS OF BORIC ACID RESULTING FROM BOILING ACIDIFIED BORIC ACID SOLUTIONS.—In keeping with the practice of boiling 50 c.c. of solution to eliminate carbonic anhydride, 50 c.c. of liquid containing sulphuric acid and a known weight of boric acid were boiled for various lengths of time. One series was carried out in a beaker flask covered with a watch glass; the other series was carried out by boiling the solution in an open shallow titrating basin, with constant stirring. The solutions were cooled, neutralised with 0.1 *N* sodium hydroxide solution, with Sofnol Indicator No. 1, and finally titrated after adding 0.5 gram. of mannitol and phenolphthalein. The volume to which the original solution was evaporated during the boiling was ascertained by pouring into a burette and measuring the contents of the vessel after titrating, and deducting the known volume of the solutions added during the neutralising and titrating.

TABLE IX.

Boric acid taken. Grm.	Time of boiling. Minutes.	Final volume. c.c.	Final titration.	
			0.1 <i>N</i> NaOH. c.c.	= H ₂ BO ₃ . Grm.
<i>Open Basin.</i>				
0.0329	5	24.7	5.30	0.0329
0.0329	10	12.2	5.20	0.0322
0.0329	15	2.0	4.58	0.0284
0.0329 to dryness		—	4.28	0.0266
<i>Beaker Flask and Watch Glass.</i>				
0.0329	5	47.3	5.30	0.0329
0.0329	10	43.5	5.30	0.0329
0.0329	15	33.1	5.30	0.0329

N.B.—In each of these tests the volume of the original solution was 50 c.c., and the acidity equal to 5 c.c. of 0.1 *N* H_2SO_4 .

From the above results it will be observed that a fair amount of liberty can with safety be taken in the process of expelling carbon dioxide from acidified dilute boric acid solutions. The boiling was found to be done most expeditiously in an open basin; 5 minutes, or even less with constant stirring, expels the carbon dioxide completely. The only likely causes of loss arise from too rapid boiling, which may cause spurting or over-drying at the edges, but this is easily remedied if constant attention is given. It was found that an appreciable loss occurred only when the solution was concentrated to about one-fifth of its original bulk, but such a condition is unlikely to occur in practice.

(To be concluded.)

The Determination of Small Quantities of Lead, with Special Reference to Urine and Biological Materials.

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I. INTRODUCTION.—For the purpose of the experimental investigation that the Committee of Enquiry on Lead Ethyl Petrol decided to carry out, a method was needed to determine small quantities of lead in a variety of substances, including urine and biological materials. It was thought that a method of determining lead giving satisfactory results with urine could be applied, with suitable modifications, to the other substances likely to be met in the course of the Committee's programme of work. The method to be described has been in use for a year, and has given satisfactory results with urine and other materials containing organic matter; and, as the details of the method are of interest to chemists, the Committee has now given permission for it to be published.

When the work was begun the only valuable method of determining lead in urine was the modified Fairhall process (*J. Biol. Chem.*, 1924, 60, 485)* adopted by the American investigators on the health hazards associated with the distribution and use of lead ethyl petrol; but, after the method to be described had been in use for several months, there came to our notice the methods of Taylor (*J. Proc. Roy. Soc., New South Wales*, 1927, 61, 315), Cooksey and Walton (*ANALYST*, 1929, 97), and Millet (*J. Biol. Chem.*, 1929, 82, 265). Taylor's method depends on the absorption of the lead in urine by calcium oxalate precipitated directly therein, but no evidence is produced to show that

* See also: "A Study of the Health Hazards Associated with the Distribution and Use of Ethyl Gasoline," 1925, p. 16, by Kehoe and co-workers, Richberg Laboratory, University of Cincinnati, Ohio, U.S.A.

the filtrate from the calcium oxalate is free from lead. The method also involves the conversion of the oxalate into carbonate by gentle ignition, a process best avoided. Cooksey and Walton's method depends on the direct electrolysis of urine, but it is not known that the whole of the lead in urine is in a form capable of carrying the electric current. Beyond repeating the electrolysis, no evidence is afforded that the electrolyte finally discarded is free from lead. Millet's method in its earlier stages is the same as that of Fairhall and, therefore, some objections to Fairhall's method would apply to it. For these reasons, and also, because the method to be described was satisfactory in practice, the three processes mentioned above were not investigated.

FAIRHALL'S METHOD.— Fairhall's method, however, as it has been so largely used, requires fuller consideration. It depends in the first place on the precipitation of the lead, together with calcium phosphate, when the urine is made ammoniacal. The precipitate is filtered on paper, dried and ashed in a muffle at 500° C., the residue being extracted with nitric acid to remove the lead. The lead is subsequently precipitated under carefully controlled conditions, first, as lead sulphide; secondly, as lead sulphate; thirdly, as lead sulphide; and, finally, as lead chromate, the precipitate in each case being allowed to stand overnight before being filtered from its solution. Finally, the lead is determined colorimetrically by making use of the reaction between lead chromate and di-phenyl carbazide, which is oxidised by the chromate radicle, giving a pink colour. The process is long, taking about six days to complete.

A consideration of the Fairhall method suggested the following points for investigation or modification:

- (1) It seemed improbable in a biological fluid, such as urine, that the whole of the lead would be in a form precipitable by ammonia. Moreover, Fairhall states that precipitation of the lead is complete only if the urine is fresh. This condition cannot always be satisfied.
- (2) It seemed desirable to avoid the risk of loss of lead by ashing at any stage in the method.
- (3) When the final lead solution is determined colorimetrically it seemed preferable to make use of a reaction dependent on the lead ion rather than on the chromate ion.
- (4) The process was too long, and a shorter method consistent with the requisite degree of accuracy was desirable.
- (5) No figures are given showing the magnitude of the error due to the presence of lead in the reagents used in the analysis, but it is stated on page 362 of "Experimental Studies on the Effect of Ethyl Gasoline and its Combustion Products" (*Bureau of Mines*, Washington, 1927) that "blank determinations should be made frequently on lead free material as a check against contamination from apparatus or reagents." Kehoe and Edgar, in *A Study of the Hazards Associated with the Sale and Distribution of Ethyl Gasoline*, 1925, p. 20, state that "lead-free reagents were employed throughout," but no mention of blank determinations is made.

The method to be described was devised, having regard to these five points. It has been tested, with satisfactory results, with urine, to which known proportions of lead in the form of lead hippurate have been added. The method was also used to show that lead is not always precipitated completely by ammonia from normal urine, even when the urine is quite fresh. This has also been shown by Taylor (*loc. cit.*).

II. OUTLINE OF THE NEW METHOD.—An outline of the method indicates how the five considerations stated above were met. The stages of the method are:

- (1) The whole of the urine is reduced to the state of a solution of inorganic salts by a process of wet combustion. This avoids the precipitation of the lead in a solution containing organic matter. Since approximately 90 per cent. of the organic matter in urine is urea, and as the salts of urea are comparatively stable, it was realised that this substance should be destroyed before attempting to remove the other organic matter by hot strong acids. This can be done by nitrous acid or an alkali nitrite, but the use of these substances was attended by some experimental inconveniences, such as an excessive volume of solution or difficulty in procuring alkali nitrites free from lead. We are indebted to Dr. Fox, Deputy Government Chemist, for the suggestion to use for this purpose, nitrosyl-sulphuric acid. The suggestion was adopted and proved entirely satisfactory in practice.
- (2) After the volatilisation of silica, separated by the process of wet combustion, the lead is precipitated from the solution as lead sulphide, together with copper sulphide, the copper having been added to aid the precipitation of the lead.
- (3) After the mixed sulphides have been washed with a solution of sodium sulphide, they are dissolved in nitric and sulphuric acids and the solution is evaporated to dryness. The mixed sulphates are dissolved in dilute nitric acid, and the solution is electrolysed, the lead being deposited on the anode as lead peroxide. This process shortens the duration of the analysis.
- (4) The lead peroxide is dissolved from the anode, and the lead is precipitated from the solution as lead sulphate, leaving behind traces of bismuth, manganese and platinum.
- (5) The lead sulphate is dissolved in a solution of ammonium acetate, and the lead in solution is determined colorimetrically as lead sulphide. This reaction depends on the lead ion.
- (6) Blank determinations were made with the actual quantities of the reagents used in each set of experiments. The magnitude of the very small "blanks" obtained is given later.

At no stage in the process is there any "ashing" of a precipitate or filter paper, these being invariably destroyed by wet combustion. Normally, the process takes three and a half days to complete.

III. TESTING OF THE METHOD.—The method has been tested and found satisfactory, both as regards its individual stages and as a whole. Experiment has shown that no loss of lead occurs at those stages in the method involving filtration, washing of precipitates or electrolysis. These stages comprise:

- (1) The precipitation of lead sulphide and the washing of it with water saturated with hydrogen sulphide. When the filtrate and wash water, to which a further quantity of copper nitrate has been added, is again saturated with hydrogen sulphide, no further precipitate of lead sulphide is obtained.
- (2) Washing of the mixed sulphides with sodium sulphide. When the sodium sulphide washings are heated with sulphuric acid and the acid solution is subsequently electrolysed, no lead peroxide is deposited on the anode.
- (3) The electrolysis. When small quantities of lead, varying from 0.015 to 1.1 mgrm., are electrolysed under the conditions to be described, the whole quantity of the lead is deposited on the anode and no lead is found on the cathode. A second electrolysis does not yield any further lead, and no lead can be detected in the electrolyte.
- (4) The precipitation of the lead as lead sulphate. The filtrate from the lead sulphate obtained from normal urines gives a coloration with sodium sulphide corresponding with quantities of lead varying from 0.003 to 0.007 mgrm. But this coloration is, in part, due to traces of platinum, and possibly also to bismuth. The possible loss of lead at this stage is, on the average, less than 0.005 mgrm.—a negligible quantity. That no lead sulphate remains on the filter paper after it has been washed with ammonium acetate, has been shown by the destruction of the filter paper by means of sulphuric acid and the examination of the resulting solution by the sulphide colorimetric process.

The whole process has been tested by the addition of known quantities of lead hippurate to urine, with the following result:

Lead (Pb) added to one litre of urine.	Lead (Pb) found.
Mgrm.	Mgrm.
0.021	0.024
0.021	0.015
0.042	0.040
0.063	0.067
0.106	0.116
0.265	0.255
0.530	0.535

Since the lead is determined finally by means of the colour produced in alkaline solution on the addition of sodium sulphide, it is essential that the solution to be

examined shall be free from all metals that give coloured sulphides. This condition is met in the following manner. All these metals, except traces of bismuth, are removed by the sulphide precipitation or by electrolysis. The lead is separated from the last traces of bismuth by precipitation as lead sulphate. Under the conditions to be described the lead can be completely separated from 1.0 mgrm. of bismuth, but this quantity of bismuth will never be present at that stage of the process, since most of it has been removed during electrolysis. The greatest quantity of bismuth found on the electrode with the lead during the progress of the work was 0.03 mgrm.

As the proportion of lead in urine is very small, it is essential to avoid, as far as possible, any adventitious gain of lead during the procedure, and, as this cannot be avoided altogether, it becomes necessary to know exactly how much lead is gained. The work was carried out in new silica vessels, and special precautions were adopted to prevent the access of dust during the process. All the reagents were specially prepared, and, wherever possible, from materials purifiable by volatilisation. A "blank" determination was made on all the reagents used for the process with each set of determinations, these being usually four in number, sometimes two, and occasionally six. Normally these "blanks" have varied from 0.002 to 0.005 mgrm. of lead (Pb), and averaged 0.004 mgrm.; in the early stages of the work three "blanks" of greater magnitude were obtained. These were 0.012, 0.013 and 0.010 mgrm., bringing the average for all the 24 "blanks" to 0.005 mgrm.

IV. PREPARATION OF THE REAGENTS.—*Water*.—The distilled water was tested periodically in portions of 1 litre, and found to be free from lead. If a metal condenser is used, care should be taken to avoid soldered joints, otherwise lead will be found in the distillate.

<i>Hydrochloric Acid.</i>	}	These were redistilled from a still made completely of clear silica ware and were stored in stoppered flasks of clear silica.
<i>Nitric Acid.</i>		
<i>Sulphuric Acid.</i>		

Hydrofluoric Acid.—This was redistilled from a still made completely of platinum and stored in a platinum bottle.

Nitrosyl Sulphuric Acid.—This reagent was prepared as follows:—Four hundred ml. of redistilled nitric acid (sp. gr. 1.4) were placed in a silica beaker of 800 ml. capacity and cooled in a bath of crushed ice. Gaseous sulphur dioxide from a syphon of the liquid substance was led into the cooled acid through a large trap consisting of an empty flask of 1500 ml. capacity, the tube dipping into the nitric acid being made of silica. The gas was bubbled slowly into the acid at such a rate that it was absorbed completely. When crystals began to form at the bottom of the beaker, the silica tube was progressively raised to prevent the incoming sulphur dioxide from coming into contact with them, since they react with sulphur dioxide to form sulphuric acid. The reaction is complete in 16–24 hours, when the liquid becomes pale green in colour. The liquor and crystals

were well mixed and divided into 5 equal portions, each of which was sufficient to destroy the urea of 1 litre of urine.

Ethyl and Amyl Alcohols.—These were redistilled from a glass still, the first and last runnings being rejected.

Citric Acid Solution.—A 10 per cent. solution of citric acid in water was made from citric acid that had been tested and found free from lead.

Ammonia (Selected).—Fifty ml. of ammonia (sp. gr., 0.88) must show no coloration on the addition of 2 drops of 10 per cent. sodium sulphide solution. It must also be free from sulphide.

Copper Nitrate Solution.—Electrolytic copper containing 0.02 per cent. of lead was dissolved in nitric acid and re-electrolysed. The deposited copper was dissolved in the minimum quantity of nitric acid, and the solution diluted until 1 ml. contained approximately 2 mgrm. of copper (Cu).

Sodium Sulphide Solution.—A 20 per cent. solution in water was made, allowed to stand for some days and then filtered. This strong solution was diluted with four volumes of water to make a 4 per cent. solution.

Ammonium Acetate Solution.—A 10 per cent. solution was made from selected specimens of the crystallised solid that were free from lead, copper, iron, and sulphide.

"Masked" Methyl Orange Indicator. (Hickman and Linstead, *J. Chem. Soc.*, 1922, p. 2502.)—One grm. of methyl orange and 1.4 grms. of Xylene Cyanol F.F. were dissolved in 500 ml. of 50 per cent. alcohol (by vol.).

Potassium Cyanide (Selected).—Ten ml. of a 10 per cent. solution must give no reaction for lead and sulphide.

Ten Per Cent. Sodium Sulphide Solution, for the colorimetric determination of lead:

Strong solution for stock:	{	Pure Na ₂ S crystals, 50 grms.
		Pure glycerin, 50 grms.
		Water to 250 ml.

This stock solution, which keeps well, was diluted with an equal volume of water before use.

V. METHOD OF SAMPLING.—The urine was collected in selected Winchester quart bottles. Seventy-two bottles, all of the same make and delivery, were chosen after tests had been made on three of them, selected at random from the 72. The tests were:—(1) In each of the three bottles were placed 50 ml. of hydrochloric acid of sp. gr. 1.1, the bottles and their contents were heated for 8 hours in a boiling water-bath and agitated at half-hour intervals. The lead dissolved by the hot acid was found to be 0.004 mgrm. (2) Fifty ml. of ammonia, of sp. gr. 0.88, was allowed to remain in each of the bottles for 8 hours, the bottles being agitated at half-hour intervals. At the end of that time no lead was detected in the ammonia.

A similar number of glass funnels, $4\frac{1}{2}$ inches in diameter, were tested in the same manner by having hot acid and concentrated ammonia poured through them repeatedly over a period of 1 hour, but no lead was detected in the acid or alkaline solutions.

The bottles and funnels were thoroughly cleansed before use by rinsing first with 250 ml. of hot dilute nitric acid (1 to 10), next with a copious stream of tap-water, and finally with distilled water. The clean, well-drained bottles and funnels were placed in padded baskets and dispatched from time to time to the source of origin of the samples.

The urine from males only was examined. It was collected directly into the bottles, transference of the urine from one vessel to another being thus avoided. A full 24-hour supply was collected in each case, usually from 3 p.m. on one day to 3 p.m. the next.

VI. DETAILS OF THE METHOD OF ANALYSIS.—(1) *For Urine*.—The total volume of the sample is measured. The drained bottle is washed with 50 ml. of hot dilute nitric acid (1 vol. of acid, sp. gr. 1.4 diluted with 9 vols. of water) until every trace of deposit has been removed from the sides and bottom of the bottle. Whenever possible, 1000 ml. of urine are taken for analysis, and to it is added its appropriate fraction of the nitric acid washings of the bottle.

(a) *Destruction of the Organic Matter*.—To 1 litre of the urine and its appropriate fraction of washings contained in a two-litre silica beaker, nitrosyl sulphuric acid, prepared from 80 ml. of concentrated nitric acid, is added gradually (*i.e.* one of the five portions obtained as described above). Repeated addition of small quantities (10 drops) of redistilled amyl alcohol is necessary to prevent frothing caused by the gaseous products of the reaction between the nitrous acid and urea. To minimise local action and consequent loss of nitrous acid, the nitrosyl sulphuric acid should be stirred frequently during its addition. The urine must, of course, be stirred constantly during the addition of the nitrosyl sulphuric acid.

When the vigorous reaction is complete, a few more drops of amyl alcohol are added, and the mixture is boiled down to about one-third of its original volume. After cautious addition of 20 ml. of redistilled conc. nitric acid (sp. gr. 1.4), the beaker is covered and the boiling continued until charring occurs, when a further 3 ml. of nitric acid are added. The heating is continued, with further additions of small quantities of nitric acid, as may be necessary, until the liquid is in a sufficiently clean state for transference to a 600 ml. beaker (any silica adhering to the large beaker should be removed by means of dilute hydrofluoric acid, as described later). After transference, a little more nitric acid is added to the diluted solution, and the boiling down is continued until sulphuric acid fumes are again evolved.

The final destruction of traces of organic matter is completed by boiling the concentrated acid solution vigorously for some time in the covered beaker, adding a few drops of concentrated nitric acid to the hot mixture, if necessary.

To ensure decomposition of residual traces of nitrosyl sulphuric acid, the warm, almost colourless, sulphuric acid solution is diluted, and again boiled

down until fumes of sulphuric acid appear. If this final dilution is omitted, the residual nitrous and nitric acids will interfere with the indicator used in neutralisation, and may prevent the complete precipitation of the lead as sulphide.

The excess of sulphuric acid is now expelled by heating until crystallisation of calcium sulphate just commences. Heating must not be continued beyond this stage, or the calcium sulphate will be rendered insoluble in water.

(b) *Removal of the Separated Silica.*—Before actual solidification takes place, the warm syrupy acid solution is diluted cautiously, first with a little cold water, and then with hot water to a volume of about 400 ml. At this stage all the calcium sulphate should be in solution, but it may be necessary to add a little hydrochloric acid and to continue heating for a short time.

The silica is now filtered off on an 11 cm. acid-washed filter paper, and washed once or twice with hot water. Any silica that remains adhering to the silica beaker is removed by means of hot water containing a few drops of hydrofluoric acid, and this solution is transferred to a platinum dish, which is covered and set aside.

The filter paper containing the silica is now transferred to a 250 ml. tall silica beaker and treated with a mixture containing 10 ml. of concentrated nitric acid, 10 ml. of water, and 3 ml. of concentrated sulphuric acid. The covered beaker is heated on the hot plate until copious fumes of sulphuric acid are evolved, when the cover is removed for two or three minutes. (*Note.*—If charring occurs, a few drops of concentrated nitric acid are added and heating continued.) The contents of the beaker are now transferred to the platinum dish, previously mentioned, a few drops of hydrofluoric acid again being used, if necessary, to ensure complete transference of silica. After the addition of 1–2 ml. of hydrofluoric acid to the solution in the platinum dish, the silica is volatilised by evaporation of the solution on the hot plate to the fuming stage. (*Note.*—In cases where difficulty has occurred in bringing about complete solution of calcium sulphate, some of which may have been filtered off with the silica, the heating with concentrated sulphuric acid in the dish must be continued until all the sulphate passes into solution in the hot concentrated acid.) Upon transference to the beaker containing the original solution, there should be no further difficulty in obtaining a perfectly clear solution.

(c) *Precipitation of the Lead Sulphide.*—To the clear colourless solution 5 ml. of a 10 per cent. solution of citric acid and 5 ml. of a solution containing approximately 2 mgrms. of pure copper per ml. are added, followed by a few drops of "masked methyl orange" indicator. Concentrated ammonia (sp. gr. 0.880) is now run in, with constant stirring, when the colour of the solution will gradually change from red to purple, and finally to a neutral greyish tint. At this point the addition of one or two more drops of ammonia will cause a change to green (P_H about 4–5), the solution being now only slightly acid to litmus. This is the degree of acidity which has been found to be suitable for the precipitation of the sulphides. Hydrogen sulphide is now passed through the solution for one hour.

After the precipitated sulphides have been allowed to settle (15–30 minutes—not longer), the supernatant liquid is decanted through an 11 cm. acid-washed

filter paper, which must be free from pinholes. Finally, the sulphides are transferred to the paper and washed twice with hydrogen sulphide water, and then with 10–15 ml. of warm (40–50° C.) 4 per cent. sodium sulphide solution to remove sulphides of arsenic, antimony and tin. If the filtrate is not quite bright, it must again be passed through the filter.

The paper containing the sulphides is now destroyed by wet combustion in a tall 250 ml. silica beaker, as described previously for the silica separation, and, when all organic matter is destroyed, the excess of sulphuric acid is expelled, the beaker being removed from the hot plate when practically all the acid has evaporated, and the remaining acid being driven off by gentle blowing, while the beaker is still hot. The lead and copper are now in the form of sulphates.

(d) *Electrolytic Deposition of Lead Peroxide.*—To the tall 250 ml. silica beaker containing the dry sulphates, 10 ml. of water are added and then concentrated (0.88) ammonia, drop by drop, until any free sulphuric acid is neutralised, this being shown by the appearance of the blue colour due to copper. Fifteen ml. of water containing 1 ml. of concentrated redistilled nitric acid are then added, and the resulting solution electrolysed, under the following conditions:—Temperature, 70–80° C.; voltage, 1½–2 volts; current density, 0.3–0.4 amps./100 sq. cm.; speed of rotation of anode, 1500–2000 revolutions per minute.

The anode is a cylinder of platinum iridium (25 per cent. of iridium) foil, 1 cm. deep and 1 cm. diameter, joined centrally to a platinum iridium wire, about 12 cm. long, and is rotated at the above-mentioned speed. The cathode is a plate of platinum iridium foil, 1½ cm. square, also joined to a wire. Before electrolysis the cathode has a thin coating of copper deposited on it electrolytically. The beaker is fitted through the lid of a water bath so that it remains suspended by the rim, the temperature of the bath being kept between 70° and 80° C. By means of a sliding resistance the voltage from a 4 V accumulator is cut down until the current through the electrolyte is 20 milliamps, this giving the correct current density. The dimensions of the beaker are such that when the electrodes are at opposite sides and this current passes, the voltage drop between the electrodes is 1.6 volts. The distance between the electrodes is then about 4 cm. The beaker is covered with a split clock-glass, and the electrolysis continued for 1 hour, after which the motor rotating the anode is stopped, and the anode removed from the solution and washed.

(e) *Precipitation of Lead Sulphate.*—The lead peroxide is dissolved from the anode in a 100 ml. tall silica beaker by heating for 30 minutes in a boiling water-bath with a mixture containing 25 ml. of water, 0.5 ml. of concentrated nitric acid, and 5–10 drops of alcohol. The anode should now be visibly free from lead peroxide, and should give no coloration when tested with Trillat's reagent (*Compt. rend.*, 1903, 136, 1205). Redistilled concentrated sulphuric acid (0.5 ml.) is now added to the solution, and the mixture evaporated on the hot plate to complete dryness (to remove all nitric acid). A further 0.5 ml. of concentrated sulphuric acid is now added, and the beaker is covered and again heated to the fuming point for a few seconds. After cooling, 15 ml. of a mixture containing 1 vol. of alcohol (about 94 per cent. by

volume) to two volumes of water are added, and *thoroughly mixed with the acid*. The mixture is allowed to stand overnight, when the lead sulphate is filtered off on a 5 cm. acid-washed, close filter paper, and washed twice with a mixture containing alcohol, water, and concentrated sulphuric acid in the respective proportions by volume 10, 20 and 1. Ten ml. of 10 per cent. ammonium acetate solution are now boiled in the beaker in which the sulphate precipitation was carried out, and the hot solution is passed through the filter into a similar beaker. This operation is repeated, the same 10 ml. of ammonium acetate being again raised to boiling, passed through the filter, and collected in the first beaker. The filter is finally washed three times with about 5 ml. of hot water containing a little ammonium acetate.

(f) *Colorimetric Determination as Lead Sulphide*.—An opinion as to the approximate quantity of lead present having been formed by inspection of the electrode after electrolysis, the whole, or a suitable proportion of the ammonium acetate solution, is transferred to a tall 50 ml. Nessler cylinder. The best quantity to be used for the matching as lead sulphide under these conditions has been found to be 0.05 mgrm. of lead. An exactly similar cylinder is used for the solution with which it is to be compared, and 10 ml. of the ammonium acetate reagent are placed in this cylinder. To each cylinder are added 2 ml. of 10 per cent. potassium cyanide solution, 5 ml. of approximately 6 N ammonia, water to the 50 ml. graduation, and, finally, with constant stirring, 2 drops of the special 10 per cent. sodium sulphide solution. A solution containing 0.01 mgrm. of lead per ml. is now run from a burette into the cylinder containing the control solution, until a match is obtained.

The solution in the cylinder containing the control is now rejected, and a fresh control prepared containing all the reagents (except the sulphide) and a volume of the standard lead solution which is less by 1 ml. than that added in the first comparison. The sulphide is added last, followed by a little more lead solution as may be necessary to produce a perfect match. The burette reading may then be recorded. The cylinders should be viewed both with the cylinder containing the control on the left and also on the right of the cylinder containing the solution to be examined.

By working with 0.05–0.10 mgrm. of lead, the results obtained colorimetrically are within 5 per cent. of the exact amount present.

(2) *FOR BIOLOGICAL MATERIALS*.—The method has been applied, with slight modification, to biological materials, the essential difference being the omission of the nitrosyl sulphuric acid. The material is first heated in a covered silica beaker with dilute nitric acid, containing 10 per cent. by volume of nitric acid (sp. gr. 1.4) until most of the solid matter has been disintegrated. The destruction of the organic matter is then completed by the action of concentrated sulphuric and nitric acids, and the process is then continued as described above.

(3) *FOR MISCELLANEOUS MATERIALS*.—Organic matter, if present, is first destroyed by wet combustion with strong nitric and sulphuric acids, the method

then being continued as described in VI (1) (b) above. It should be noted, however, that the presence in the electrolyte of relatively large quantities of iron salts causes an incomplete deposition of the lead during electrolysis. If, on neutralisation of the electrolyte during the process of adjusting the acidity of the solution prior to electrolysis, a red precipitate of ferric hydroxide should be observed, it is advisable to reverse the sequence of the electrolysis and the separation of the deposited lead as lead sulphate.

VII. RESULTS.—Fifty-five samples of normal urine from persons residing in London and the surrounding country districts gave quantities of lead varying from nil to 0.133 mgrm. of lead (Pb) per litre, the average value being 0.040 mgrm. of lead per litre.

We wish to thank Sir Frederick Willis, K.B.E., C.B., Chairman of the Committee of Enquiry on Lead Ethyl Petrol, for permission to publish the work described in this paper, and also Sir Robert Robertson, K.B.E., M.A., F.R.S., the Government Chemist, for constructive criticism and advice.

THE GOVERNMENT LABORATORY,
CLEMENT'S INN PASSAGE, LONDON, W.C.2.

Official Appointment.

THE Minister of Health has confirmed the following appointment :

MR. A. E. JOHNSON, B.Sc., F.I.C., as Public Analyst for the County Borough of Wolverhampton (November 11, 1929).

Notes.

The Editor wishes to point out that the pages of the Journal are open for the inclusion of short notes dealing with analytical practice and kindred matters. Such notes are submitted to the Publication Committee in the usual manner.

STEROLS IN BUTTER.

DR. VAN SILLEVOLDT, Director of the Dutch Dairy Station at Leiden, has kindly given me permission to publish the following process for separating the sterols from butter and similar fats. The process, which was devised by the Director, in association with the members of the staff of the Dairy Station, was given to me in April, 1928, and, since then, I have found it to be of great use in the examination of butter, especially of small samples.

Process.—Saponify, with reflux condenser, 15 grms. of filtered fat with 9.5 ml. of potassium hydroxide solution (1000 grms. of KOH in 1400 ml. of water) and 20 ml. of alcohol (96 per cent.) in a 300 ml. conical flask. Shake while warm until the fat is dissolved, and heat further for half-an-hour.

Cool, add 60 ml. of water and 180 ml. of alcohol (96 per cent.), mix, and add 10 to 20 ml. of digitonin solution (1 per cent. of Merck's digitonin in 96 per cent. alcohol). Allow the mixture to stand for 24 hours in a cool place and filter on Buchner funnel with a closely-fitting paper. Wash with a small amount of alcohol to remove soap. The digitonin-sterol compound flakes off on drying. Weigh the steride and acetylate it with ten times its weight of acetic anhydride, and proceed with the crystallisation from alcohol (about 95 per cent.) as in the Bömer method.

A. MORE.

THE FALL IN REICHERT-MEISSEL VALUES ON KEEPING BUTTER SAMPLES.

THE following figures may be of interest as showing how the Reichert-Meissl values of five samples of butter decreased after having been kept for nearly six years in bottles fitted with metal screw caps and cork discs. From the condition of the caps it appeared possible that a slow renewal of the air in the bottles might have taken place by diffusion, and, owing to temperature changes, over a prolonged period. The original samples were genuine butters with abnormally low Reichert-Meissl values, and moisture percentages ranging from 12.4 to 14.7.

It will be noted that there is a parallel between the amounts of free fatty acids formed, and the corresponding losses in volatile acids, suggesting that the former might possibly be taken as an index of the latter.

Sample No.	R.M. values of the fresh samples.	The same samples nearly 6 years old.				
		Free fatty acids. Per Cent.	R.M. value.	Polenske value.	Kirschner value.	Saponification value.
1	20.7	27.0	8.0	1.3	7.1	211
2	21.8	14.5	16.5	1.6	11.9	224
3	20.7	14.0	15.8	1.3	12.4	224
4	21.1	7.5	19.5	2.2	14.4	231
5	21.5	6.0	20.8	2.0	15.2	230

PAUL ARUP.

BUTTER TESTING STATION,
DUBLIN.

FURFURAL IN HEATED HONEY.

IN the paper entitled "Furfural and Diastase in Heated Honey" (ANALYST, 1929, 381), we stated that the tests on the possible development of furfural in heated honey due to storage were being continued. These tests have now been completed. In the case of the samples cited on page 387:—

Samples described under (a) still gave negative aniline acetate and Fiehe tests after storing for 12 months.

Samples described under (b) still gave negative aniline acetate and Fiehe tests after storing for 8 months.

Samples described under (c) still gave, after continued storing for 9½ months, the same results in the aniline acetate and Fiehe tests as directly after heating.

Moreover, in all cases, samples of the same honey, unheated, were kept side by side with the heated samples; these also produced no furfural.

CONCLUSION.—These further results indicate that no furfural or furfural derivatives are developed when heated honey is stored for periods up to 12 months.

L. H. LAMPITT.
E. B. HUGHES.
H. S. ROOKE.

FURTHER EXPERIMENTS ON THE ACTION OF AIR ON FLOWERS OF SULPHUR AND GROUND SULPHUR.

IN view of the suggestion that the results previously recorded (ANALYST, 1929, 590) might have been due to the ground sulphur being coarser than the corresponding samples of flowers of sulphur, the following further estimations were carried out on a sample of ground sulphur which was finer than the flowers of sulphur originally employed.

The sample of flowers of sulphur used in the previous estimations showed 98.5 per cent. passing a 300-mesh sieve, and the one used in the following estimations showed 100 per cent. passing a 300-mesh sieve.

The results obtained were as follows:

Class of sulphur.	Weight of sulphur taken. Grm.	Temperature. °C.	Vol. of air. Cb. ft.	N/100 iodine. c.c.	Equivalent to SO ₂ on weight of sulphur taken. Per Cent.
Ground	1	60	1	Nil	Nil
Ground	1	80	1	Nil	Nil
Ground	1	90	1	0.2	0.0064
Ground	1	100	1	1.3	0.0416

These results are practically identical with those previously recorded, and confirm the inactivity of ground sulphur at lower temperatures in comparison with flowers of sulphur.

J. E. STEPHENSON.
S. W. BRIDGE.

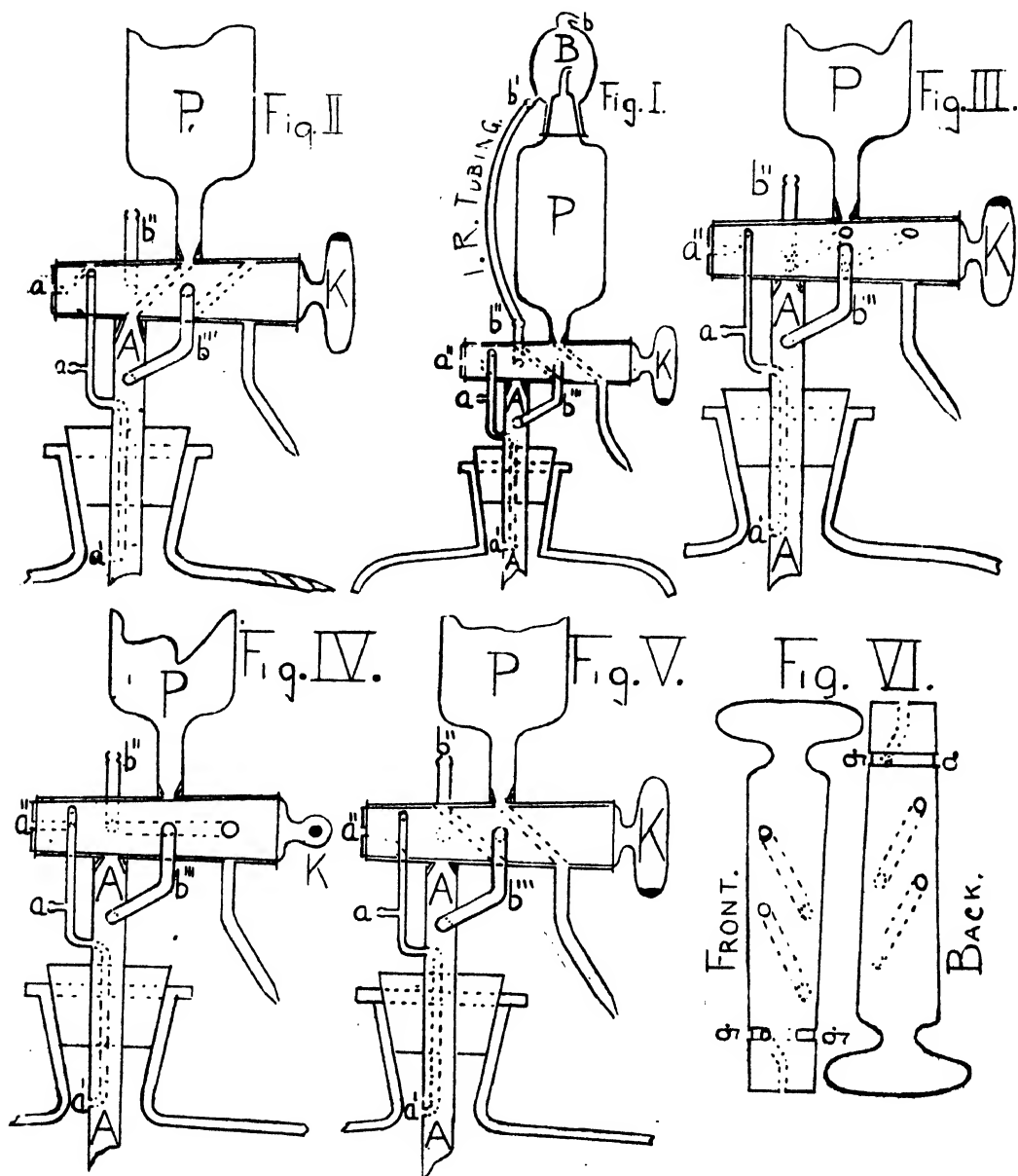
AUTOMATIC PIPETTE.

THIS form of automatic pipette is intended for filling by means of air-pressure and for fitting on to large storage-bottles, as shown. Ordinarily, the necessary pressure is obtained by the use of a small hand-bellows. If desired, however, a slight additional transverse surface-grooving of the key will permit the using of a small-power mechanical blower (g. Fig. VI).

From the diagrams it will be seen that:

- (i) All the movements involved in the use of the pipette are under the control of a single key, and
- (ii) single-necked storage bottles and one-hole stoppers suffice.

MANIPULATION.—A one-hole stopper having been fitted (as shown) on the stem A of the pipette and fastened securely in position in the neck of the storage-bottle, the bellows is joined up at *a*, and the pressure inside the bottle is increased by way of *a* and *a'* (Fig. I).



(1) The key K being set as in Fig. II, the liquid rises in A, then through the key and the pipette-body P, to overflow into the bulb B (Fig. I). Should B overflow, excess of liquid will run off through *b*, fitted with a suitable length of rubber-tubing, into a beaker or a sink. *The free end of this tubing must not dip under liquid.*

(2) P being filled to overflowing into B (Fig. I) the key is turned forward (the end marked black in the diagram towards the operator) into the position shewn in Fig. III. This

- (i) disconnects P from the storage-bottle, and
- (ii) connects the bellows and storage-bottle with the external air by means of *a*, *a'* and *a''*.

(3) Air-pressure inside the storage-bottle being again normal, K is continued forward into the position shown in Fig. IV:

- (i) The overflow in B (Fig. I) runs back into the bottle by way of *b'* (Fig. I), rubber-tubing, *b''*, the key, and *b'''*.
- (ii) The tip of the pipette-body is left clear of overflow.

(4) K is again continued forward into the position shown in Fig. V, and P is thus connected with the receiving vessel into which it discharges.

On turning back the key into the position in Fig. II, the operator is again ready to begin a measurement.

Should the operator consider that attaching a bellows at *a* might lead to fracture of this part of the pipette through an accidental jerk, *a* may be closed and the bellows connected with the air-space of the store-bottle by means of a glass elbow of small-bore tubing which is fitted into a second hole in the stopper.

The apparatus is made by McCulloch Bros. and Wilson, 46A, West Princes Street, Glasgow, C.4.

UNIVERSITY OF GLASGOW.

A. HENDERSON.
J. ROBERTS.

Notes from the Reports of Public Analysts.

The Editor would be glad to receive the Annual or other Reports of Public Analysts containing matter of special interest to the Society. Notes made from such Reports would be submitted to the Publication Committee.

CITY OF LEEDS.

REPORT OF THE CITY ANALYST FOR THE SECOND AND THIRD QUARTERS, 1920.

THE total numbers of samples examined in the two quarters were 731 and 713, of which 523 and 494, respectively, were samples taken under the Food and Drugs Acts. Of these, the percentages adulterated were 14.3 and 14.8.

MILK.—One hundred and thirty-seven of the 724 samples of milk were adulterated or below standard. It is significant that one of the worst cases of fat deficiency (19 per cent.) was a Grade A milk. Fat deficiency in Grade A milk is partly due to the practice of bottling milk from individual cows instead of bottling

the mixed product of the whole herd. Where the herd is a Friesian one, the fat deficiency is liable to be more pronounced than in the case of other herds. In these instances the public are paying an increased price for milk which, though it has to conform to a bacteriological standard not demanded of ordinary milk, is nevertheless inferior to the latter as regards its chemical composition.

CREAM BUNS.—Of 5 samples submitted, 4 contained imitation cream filling. In one case this consisted of a mixture of 75 per cent. of cane sugar and water with 25 per cent. of fat, which was composed of 97 per cent. of palm-kernel oil and 3 per cent. of butter fat.

In a second case coconut oil was the predominant oil, but in this case, as in the remaining two, the quantity of fat available for examination was insufficient for a full analysis. In the remaining two cases fats with low Reichert and Polenske values had been employed. In the case where butter fat only had been used in conjunction with cane sugar and water, the proportions were as follows:—Water, 9·6; cane sugar, 17·9; butter fat, 72·5 per cent.

Legal advice has been taken concerning imitation cream used as a filling, and is to the effect that the Artificial Cream Act, 1929, does not cover this. Hence, as none of the buns in question contained boric acid, they have been returned as genuine. (Cf. ANALYST, 1928, 53, 383.)

C. H. MANLEY.

CITY OF SALFORD.

ANNUAL REPORT OF THE CITY ANALYST FOR THE YEAR 1928.

THE total number of samples (1484) is greater than that for any previous year, with the exception of 1924, and represents a purchase of 593 samples per 100,000 of the population, which is a greater number than that taken by most other local authorities. Of the total samples, 70, or 4·72 per cent., were returned as adulterated. The number of informal samples was 751.

MILK.—During the year 1103 samples were examined, of which 43 (3·9 per cent.) were returned as adulterated.

Abnormal Milk.—During the first quarter a number of samples from different farms gave a percentage of solids-not-fat below the legal standard. These samples came from so large a number of different farms that it was evident that it was not so much a question of adulteration as of natural variation. No action was, of course, taken, since it was obvious that these samples were as they came from the cow. No reason can be assigned for this unusual state of affairs, but there is a possibility that it may be connected in some way with the extraordinary rise in the percentage of fat during the last four months of 1927, which continued into the first three months of 1928. The average fat figures for all milk samples during these seven months were as follows:

September	4·21
October .	4·25
November	4·14
December	4·05
January . .	3·92
February .	3·68
March .	3·81

These figures are very seldom equalled either in Salford or anywhere else, and our knowledge of the cow's physiology is not so complete as to be able to

assign a reason for this phenomenon. There is at least a possibility that there may be some sort of relation between it and the, quite as unusual, drop in solids-not-fat. At least two other Public Analysts in this district experienced the same sort of thing, and no reason could be assigned in these cases.

CHEESE.—Eighteen samples of Cheshire cheese contained from 49 to 60.3 per cent. of fat (calculated on the dry substance). Cheshire cheese should contain at least 45 per cent. of fat (on the dry substance).

Bondon Cheese.—One sample of "Bondon" cheese contained only 0.8 per cent. of fat and 72.1 per cent. water. There is, however, no standard for this type of cheese, although it seems originally to have been a whole-milk cheese. A large section of the dairy industry are now making it from skimmed milk, and consider the practice perfectly legitimate.

Full-Cream Cheese.—A sample labelled "full cream" cheese was bought by the inspector as cream cheese, but, on analysis, it was found to be an ordinary whole milk cheese. A representative of the firm, when interviewed, said that he thought that it was a cream cheese. It was pointed out to him that, although the term "full cream" might, in the trade, signify whole milk cheese, it would be taken by the ordinary purchaser to signify a better article, particularly as the price was higher than that of other cheeses sold in the shop. The firm agreed to substitute the words "pure rich" for "full cream" on the labels of this cheese.

Standards for Cheese.—Although power is given under the Food and Drugs Act to make regulations as to the composition of cheese, this power has, as yet, not been exercised. A fairly definite standard has now been adopted for Cheshire cheese, but this is only one variety out of many.

Home-made Lemon Cheese.—Fines were imposed on the vendor and makers of an article described as "Home-made Lemon Cheese," the Stipendiary remarking that home-made articles should be made from ingredients such as the house-wife would use. (See ANALYST, 1929, 105.)

WHISKY.—A sample was found to be 43.6 degrees under proof, and proceedings were instituted against the vendor, who was fined £5. It was discovered that this whisky had been bought from a wholesale spirit merchant and invoiced to the retailer as 40 degrees under proof. The wholesaler was interviewed, and in conversation admitted that he was responsible for the labelling of the bottles, and also that the spirit was nominally 45 degrees under proof. A summons was thereupon taken out against him under Sec. 27 of the 1875 Food and Drugs Act, the relevant part of which states that "Every person who shall wilfully give a label with any article sold by him which shall falsely describe the article sold shall be guilty of an offence, etc." In this case it was possible to prove both that the actual composition of the article was known to the person giving the label and that the label was wilfully given by him. It is not often that this can be done in such cases.

The case was adjourned by the Stipendiary for the attendance of either the actual proprietress or her legal representative, and at the adjourned hearing it was submitted that the label was false, inasmuch as it described as whisky, without any qualification, spirit which had been diluted below the strength of 35 degrees under proof. This rather novel submission was upheld by the Stipendiary, and the defendant was fined £15 and 30s. costs.

COD-LIVER OIL TABLETS.—In addition to the case in which the defendants were fined £30 and 75 guineas costs (ANALYST, 1928, 53, 336), there have been several instances of misdescription of cod-liver oil tablets. A sample of one brand was advertised as containing the "active principle of the liver in a palatable form," and it was also stated that each tablet was equivalent to a tablespoonful of cod-liver oil. Examined by the colour test, five tablets were found to contain less vitamin A than one drop of ordinary commercial cod-liver oil. The firm, when interviewed, agreed to discontinue the sale of these tablets.

Another brand, which contained vitamins *A* and *D* in good proportion, bore on the label the statement: "Each tablet is equal to a spoonful of the finest cod-liver oil." Since to state that a tablet which contains merely a vitamin-containing portion of the oil is equal in value to the oil itself, is obviously untrue, the firm was communicated with and agreed to substitute the phrase: "These tablets contain vitamins *A* and *D* extracted from the finest cod-liver oil."

Another sample represented a brand which was advertised to be "250 times as rich in vitamins as the best butter." Vitamin *A* was found to be practically absent, five tablets containing less than does one drop of cod-liver oil. The firm promised that the article would no longer be manufactured.

PROPRIETARY MEDICINES.—Under existing law the sale of worthless proprietary medicines cannot be prevented. Under Sec. 2 of the Food and Drugs (Adulteration) Act, 1928, proprietary medicines are specifically exempted from the Act; the prosecution for the sale of cod-liver oil tablets is probably the first case of its kind, taken under the Food and Drugs Acts, which has succeeded. Had the article been asked for under the proprietary name of "——'s Cod-Liver Extract Tablets," there would have been no case, since the purchaser would have got precisely what he demanded. But inasmuch as cod-liver oil tablets, which are not proprietary, were asked for, and the proprietary article was supplied, a case could be brought, though the question whether the sub-section, dealing with proprietary medicines, was still operative, was not raised by the defendant.

This country is practically the only civilised country in the world which has no means of controlling these articles; and, in view of the immense amount of harm that may be caused by them, this lack of control is a national disgrace. As an example of the state of British, as compared with foreign, law on the subject, it may be of interest to mention that one person is said to have made a profit of £60,000 in this country by advertising and selling an alleged vibratory cure for many diseases, whereas, for the same procedure in France, he was fined £120 and sentenced to three years' imprisonment.

H. H. BAGNALL.

Legal Notes.

Under this heading will be published notes on cases in which points of special legal or chemical interest arise. The Editor would be glad to receive particulars of such cases.

PRESERVATIVE IN MEAT. REFUSAL OF WARRANTY BY WHOLESALE.

ON August 28, a firm of butchers was summoned at Wimbledon for selling beef which contained 0.022 per cent. of sulphur dioxide, contrary to Sec. 2 of the Food and Drugs Act, 1928.

Mr. Beck, for the defence, submitted that there was no case to answer, since there was no evidence of fraudulent intent. The meat was sold in exactly the same condition as when it was received from the Smithfield market. The Smithfield dealers refused to give a guarantee that the meat sold complied with the Preservatives Regulations. Since the regulations came into force no preservatives had been purchased or used in the shop at Wimbledon. A modern meat safe had been installed, and only sufficient meat for the daily trade was bought.

The Chairman said that the Bench was agreed that there had been no fraudulent intent, and had decided to dismiss the case.

Mr. Hart, for the Surrey County Council, asked if the Bench would be prepared to state a case for appeal on the point of law that had been raised.

OBLITERATION OF ORIGIN MARKS FROM EGGS.

ON October 21, the adjourned summons under the Merchandise Marks Act against an egg dealer was heard before the Hull Stipendiary magistrate.

An inspector of the Hull Corporation gave evidence that, on visiting the defendant's premises, he had found one of the rooms partitioned off and provided with means for washing eggs. Three employees were there, and he noticed two receptacles, one of which contained sulphuric acid. Witness asked the employees if they were engaged in rubbing the marks off the eggs. One girl replied "Yes," another "No," and the boy did not answer the question. Witness later purchased some marked eggs at 1s. 4d. per dozen, and others marked "Guaranteed English eggs," at 1s. 8d. per dozen, which was 2d. per dozen below the wholesale price, and these eggs had obviously been washed.

Mr. A. R. Tankard, F.I.C., Public Analyst, said that he had examined a number of eggs which had been purchased from the defendant. Some of them which were unmarked gave abundant evidence of sulphate, and showed traces of purple spots and smears. Three eggs of another batch (from the shop) had originally been marked in purple, and, in his opinion, had been treated with sulphuric acid. The two bottles of liquid submitted consisted of dilute sulphuric acid of 0.17 and 0.84 per cent. strength, and both contained a deposit of calcium sulphate.

The defendant said that the eggs were often dirty, and his employees were provided with materials for washing them; after washing they were re-stamped. He had a stamp marked "Holland."

In reply to the Magistrate, he said that, although he also bought eggs from Russia, France and Belgium, he stamped all of them, after washing, with the "Holland" stamp.

The Stipendiary Magistrate said that the defendant had not discharged the onus of proof that the cause for the removal of the marking had not been for the purpose of concealing the origin of the eggs at the time of their sale.

He inflicted a fine of £5, with ten guineas costs.

Department of Scientific and Industrial Research.

FOOD INVESTIGATION. Special Report No. 35.

HEAT INSULATORS.*

THE function of insulating materials such as granulated cork, charcoal or slag wool is to subdivide the air space into such small cells that convection is reduced to the maximum extent and transmission of heat through a wall of granulated material is the composite effect of conduction, radiation and convection.

Experiments described consist in a quantitative measurement of the thermal conductivity of various materials, which is defined on the British system as the quantity of heat in B.Th. Units which flows per sq. ft. per hour through 1 in. thickness of material for a difference of temperature of 1° F. between the faces. This number is 2903 times that which would express the same conductivity on the C.G.S. system.

* Obtainable from H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 2s. 6d. net.

The apparatus used consists essentially of a central hot plate and a guard ring round it of an outer plate in the form of a ring in the same plane with the central part, but separate, and maintained at the same temperature. The hot plate is fixed centrally between two cold plates, and the material under investigation is packed between. The heat transmitted is measured as watts dissipated in the hot place, and the temperature difference is observed by means of a number of thermocouples attached to various points on the hot and cold faces. Several sets of this apparatus were used, 5 ft. 20 in. and 12 in. The apparatus is filled with the material which, if compressible, is adjusted to the density of packing desired, the heat supply switched on and adjusted till the specified temperature of the hot plate is obtained. The temperature of the guard ring is equalised and the apparatus left undisturbed with a constant energy supply from battery to hot plate, and observations of temperature are made about every 12 hours until a steady state is obtained. The temperature difference, average temperature of faces, and the calories per sq. cm. per second per 1 cm. thickness are worked out.

A study of convection currents shows that the phenomenon of the transfer of heat from a vertical hot wall is more complicated than has been supposed, and, in estimating effects of convection, account must be taken of the altered character of the flow of air along the surface.

Details of experiments on some 40 different materials tested include the following figures for B.Th.U. per sq. ft. per hour for 1 in. thickness and 1° F. difference in temperature, and the mean temperature of the insulating material:—Slab cork, 0.28, 46°; granulated cork, 0.29, 32°; sample baked, 0.25, 177°; coarsely granulated cork, packed, 5.4 lb. per cu. ft., 0.32 to 0.35, 23°; cork wool, treated with paraffin, 0.22, 48°; charcoal, 0.34, 63°; fibre from bark of eucalyptus tree, 0.32 to 0.38, 32°; rubber sponge sheet (24 lb. per cu. ft.), 0.37, 95°; teak, 0.81, 81°; eel grass, 0.31, 86°; concrete block, 8.1, 88°.

The value 0.29 B.Th.U. per sq. ft. per hour per 1 in. thickness for 1° F. difference of temperature between the faces is regarded as representing the thermal conductivity of an insulating material of good quality. Finely granulated cork after baking to a dark brown colour is a better insulator than the raw material, and coarsely granulated cork is not so good; cork wool or cork shavings are very good insulators, but, in practice, the material would have to be protected from access of moisture. Dry charcoal is good, but the moisture-absorbing powers are a great drawback. Of timbers, the light wood "balsa" combines efficiency with some facility for being cut into shape, but it is soft; crude diatomaceous earth and granular pumice have conductivity coefficients about twice that of slab cork.

Experiments on the moisture-absorbing capacities of insulating materials are described where the materials are in equilibrium with air of various humidities, and where they are immersed in water. The determination of specific heats of insulating materials is described, as the constant is important when calculations have to be made of heat transmission through walls, before the steady state has been attained. The mechanical properties of slab cork are dealt with in detail.

D. G. H.

References to Scientific Articles not Abstracted.

PHOTOMICROGRAPHS OF PHILIPPINE STARCHES. By R. N. ALLEN.

THESE appeared in the February issue of the *Philippine Journal of Science*, 38, 241. (Cf. ANALYST, 1929, 686.)

Report of the Chief Inspector of Factories and Workshops, 1928.

INDUSTRIAL DISEASES.*

IN addition to industrial diseases of a well-recognised type, attention is directed to others arising from the use of chemical substances hitherto little known outside the laboratory.

LEAD POISONING.—This showed a decrease (326 cases notified and 43 fatal). Two cases were attributed to the use of "flake white," which is practically entirely composed of lead carbonate, and hitherto has not been labelled "lead."

ARSENICAL POISONING.—Two fatal cases of arsenical poisoning were due to (1) accidental ingestion of arsenical sheep dip, and (2) ulceration caused by arsenic in emerald green, etc., extending over some years. An examination of 14 men in contact with a powder containing arsenic and an alkali, disclosed circumscribed ulceration in 4, effects on the nasal septum in 7 and well marked dermatitis in 12.

MERCURIAL POISONING.—Of 4 cases of mercurial poisoning, 3 occurred in the manufacture of thermometers and 1 of electric meters.

ANILINE.—Since 15 of the 41 aniline poisoning cases occurred in June, July and August, the influence of hot weather is to some extent indicated. One of the most severe cases was due to accidental splashing of clothing with aniline oil, and another case to use of an ink remover containing aniline oil.

HYDROGEN ARSENIDE.—Inhalation of arseniuretted hydrogen accounted for 6 toxic poisoning cases, and other cases were due to escapes of the gas which were not anticipated. In one, saw-dust was mechanically stirred in an open tank containing molten tin, and 10 of 15 men present were affected; an analysis of the skimmings from the tank showed 0.29 per cent. of arsenic.

HYDROGEN SULPHIDE.—Nine cases of hydrogen sulphide poisoning (3 fatal) were reported, two being due to the charge of sulphuric acid being run too quickly into a vat containing sodium sulphide solution.

ANTHRAX.—Three of 24 anthrax cases proved fatal, the increase of cases being due to increased importation of infected hides from China. Drs. Jordan Lloyd and Robertson are studying methods for disinfecting the hides, and a laboratory method making use of a sulphonated oil in conjunction with a disinfectant, is being worked out.

DERMATITIS.—This is not notifiable, but 662 cases were referred, showing a steady increase, which indicates that increased importance is being attributed to the condition. Paraffin, turpentine and methylated spirits, as well as alkalis, are used to cleanse hands and arms after work, and unless these agents are themselves removed very thoroughly, they are liable to cause dermatitis.

D. G. H.

* Obtainable from H.M. Stationery Office, Adastral House, Kingsway, W.C.2. Price 2s. 6d. net.

Ministry of Agriculture and Fisheries.

EGG PRESERVATION AND THE REGISTRATION OF PREMISES.

THE following Press notice has been issued by the Ministry:

It is clear, from information which continues to reach the Ministry from time to time, that in some quarters the provisions of the Agricultural Produce (Grading and Marking) Act, 1928, regarding the registration of premises used for the preservation of eggs are not yet fully understood. The position may be briefly summarised as follows:—

For the purposes of the above Act, the various processes for preserving eggs have been divided into two classes:—

- (a) Those the use of which can subsequently be detected by chemical analysis, because the composition of the shell has been altered by the pores of the shell having become filled with the preserving material; and
- (b) those that cannot be so detected because the shell is not affected in any way.

Processes such as immersion in lime-water, water-glass or oil come into the first category, and therefore under the operation of Section 3 of the Act. Premises used for the preservation of eggs by such processes are *not required to be registered*.

The only processes in the second category at present employed in this country on a commercial scale are cold storage and chemical storage, *i.e.*, storage in a gas. British eggs so preserved come within the scope of Section 4, and must not be moved from the place of storage unless each egg is marked in the prescribed manner. Premises used for the cold storage or chemical storage of eggs *are required to be registered* under Section 4 of the Act by, as regards England and Wales, the council of the county or county borough (or in the case of the administrative county of London by the Common Council of the City of London or the Council of the Metropolitan Borough) in which the premises are situated.

Queensland.

REPORT OF THE GOVERNMENT ANALYST FOR THE YEAR ENDING JUNE 30TH, 1929.

DR. J. B. HENDERSON, in his annual report, states that the total number of samples examined during the year was 6858, of which 1986 were for the Health Department, and 1568 for the Customs. Of the samples for the Health Department, 766 were formal samples taken in accordance with the Health Acts, and 237 of these were condemned as adulterated or below the standards.

MILK.—Of the 715 legal samples, 506 passed the standard and 57 were genuine, but below the standard.

The improvement in the milk supply during 1927–28, as compared with other years, has unfortunately not been maintained; in fact, the proportion of adulteration this year is much higher than it has been for many years. The only redeeming feature of the position is the continued improvement in the cleanliness of the supply, as adjudged from its comparative freedom from visible dirt and from bacteria.

Nearly 8 per cent. of the samples received were genuine milks which failed to conform with the legal standard for milk. Probably nowhere else in the British Empire is the milk vendor so thoroughly safeguarded from unfair prosecution as in Queensland. Only results from fresh samples are accepted for the purposes of legal prosecution, and the umpire sample is kept in cold storage, so that it will be in a fresh condition for analysis when required.

THE FREEZING-POINT TEST.—For more than twenty years the freezing-point test has been used in the routine examination of milk in this laboratory. Following a paper on this subject which Dr. Henderson read before the Queensland Royal Society in 1909, the Dominion Laboratory of Wellington, New Zealand, investigated and adopted the freezing-point method for determining added water in milk, and has now employed it for fifteen years with eminently satisfactory results. According to a recent report from that laboratory, the maximum variation in the freezing point of milk is from -0.545° C. to -0.565° C. Only one out of 270 samples recorded above -0.55° C. These results confirm those obtained in the Queensland Government Laboratory, and those of many other observers in other parts of the world. Dr. Monier Williams reported in 1912 to the Local Government Board of Great Britain that the freezing point is "the most constant of any of the properties exhibited by milk." This capable observer, however, retarded general adoption of the method in Great Britain by stating that "owing to the experimental difficulties involved in obtaining reliable results, it is somewhat doubtful whether the method is capable of general application for purposes of milk control." In Queensland, however, the mechanism of the test has been reduced to such simplicity that any ordinarily trained observer can determine the proportion of adulteration to within one per cent. of the truth.

LEAD ARSENATE IN CABBAGES.—In last year's annual report it was noted that arsenate of lead had been found in cabbages in dangerous proportion. The Food and Drugs Regulations provide for no arsenic or lead in vegetables. A number of growers, particularly in one district, took no notice of the warnings given, and a number of consignments of cabbage contaminated with arsenate of lead have been seized in the markets and destroyed. Many of these cabbages contained comparatively high amounts of arsenate of lead, four containing between fifteen grains and seventeen grains. One, on which the white stains of arsenate of lead were freely visible, was boiled with salt and a little soda exactly as in an ordinary household. After straining, it was found, on analysis, that the arsenate of lead, as a result of the boiling, had become evenly distributed throughout the cabbage and the water. The total arsenate of lead present was fifteen grains. An ordinary helping of about three ounces of this cabbage would contain 0.25 grain of lead (calculated as metal) and 0.375 grain of arsenic (calculated as As_2O_5). Children are being advised at school to drink a cupful of cabbage water when they get the chance—probably for the vitamin content. A cupful (say nine ounces) of water from this cabbage would contain 1.1 grain of lead (calculated as metal) and 0.6 grain of arsenic (calculated as As_2O_5), and the maximum medicinal dose of arsenic for an adult is only 0.06 grain. It is quite evident that there must have been cases of fairly acute poisoning from some of these cabbages. The symptoms of gastric and intestinal irritation in such cases occurring after a meal would not unlikely and not unnaturally be classed as "ptomaine poisoning." There would also be a certainty of chronic lead poisoning if such contaminated cabbages were regularly used as a food. The drastic but necessary destruction of contaminated consignments will probably put an end to this highly dangerous practice.

LEAD IN SODA WATER.—Of 119 samples of soda water examined, 69 samples contained lead in the proportion of 1/100th grain or more per gallon. While the proportion of lead has been markedly reduced since 1926–27, it is important, from a health standpoint, that soda water should be entirely free from such a toxic substance as lead. It would be interesting to know if the country that is supplying carbonators containing lead solder to Australia is also providing its own inhabitants with soda fountain drinks containing lead in solution. Queensland and Palestine

are the only countries, so far, where we have seen the presence of lead in soda water reported.

ORANGE CORDIALS.—Of twelve samples of orange cordials examined, seven passed the fruit cordial standard, which requires the presence of not less than 20 per cent. of fruit juice. The aerated orange beverages on the market contained from nil to 10 per cent. of orange juice. The orange drink stalls were found to be dispensing a beverage containing about 10 per cent. of orange juice. It is important, from the aspect of national health and the interests of our orchardists, that the use of pure fruit drinks should be fostered in every possible way. A regulation appears to be necessary, stipulating for a minimum proportion of, say, 5 per cent. of orange juice in orange beverages, and the elimination of preservative and artificial colouring from all drinks sold over the counter for immediate consumption and purporting to be made on the premises from fresh fruit juice.

MINCED MEAT.—Of twenty-two samples of minced meat and sausages examined, thirteen failed to meet the standard in regard to preservative, the excess of sulphur dioxide in the sausages ranging from 2 to 243 per cent. Preservative is now forbidden in minced meat.

CHEWING GUM.—Three samples of chewing gum contained drugs in the form of acetylsalicylic acid and phenolphthalein. This method of administering drugs is undoubtedly dangerous.

FLESH-REDUCING SOAP.—A sample of soap, sold at a fabulous price, and described as flesh-reducing, was found to be ordinary toilet soap adulterated with talc. A liquid preparation for reducing adipose tissue consisted of alcohol, soap and camphor. The selling price of this simple mixture worked out at nearly £5 per pint.

ANILINE DYES IN PAINTS.—The samples of paints examined were mainly those tendered to the State Stores Board, and advice was given as to the relative qualities and values. A most objectionable practice has recently been adopted by certain manufacturers, of adding aniline dyes in different proportions to some of the paints. These dyes are being fairly freely used in the reds, browns, and stone colours, and have been met with in the green. They are not lasting in daylight, and paints tinted with them must alter in colour comparatively soon after being applied. All such paints have been rejected for Government use. A case, not that of a Government building, was recently brought to the notice of the Government Analyst, where a house which had been painted a light stone colour had bleached to white in three months wherever strong light fell on the paint.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS.

Food and Drugs Analysis.

Examination of Honey. J. Fiehe and W. Kordatzki. (*Z. Unters. Lebensm.*, 1929, 58, 69-76.)—Further comparative experiments (*cf.* ANALYST, 1929, 108, 241) have been made on methods for the determination of oxymethylfurfural in honey, and the following modification of Troje's method (*loc. cit.*) has been thoroughly tested and found to give the most reliable results. A solution

of 100 grms. of honey in 400 c.c. of water is shaken with 5 c.c. each of 30 per cent. zinc acetate and 15 per cent. potassium ferrocyanide solutions, filtered, and extracted with 50 c.c. of ether. The extract is shaken with 50 c.c. of petroleum spirit and 10 grms. of anhydrous sodium sulphate, evaporated at a low temperature after 24 hours, and the residue extracted with 20 c.c. of water. For the iodine method an aliquot part of the honey solution (sufficient to leave at least two-thirds of the iodine unconsumed) is mixed with 10 c.c. of 0.1 *N* iodine solution, and diluted to 100 c.c., the alkalinity being adjusted to 0.5 *N*. After 2 hours 25 c.c. of *N* sulphuric acid are added, and the solution titrated with 0.1 *N* thiosulphate solution (1 c.c. 0.1 *N* iodine solution = 677 mgrms. of oxymethylfurfural). For the phloroglucide precipitation the authors add 30 c.c. of a 0.625 per cent. solution of diresorcinol-free phloroglucinol in 16 per cent. hydrochloric acid to 10 c.c. each of honey extract and 32 per cent. hydrochloric acid. After 24 hours the precipitate is filtered off, washed with 20 c.c. of water in 5 c.c. portions, dried at 100° C. for 3 hours and weighed. Then 2, 5, 10, 15, 20, 25, 30 and 36 mgrms. of phloroglucide correspond with 2.3, 4.2, 5.9, 7.9, 9.9, 12.0, 14.0, and 16.3 mgrms. of oxymethylfurfural, respectively. Lenk's method (*loc. cit.*) depends on the reduction of an alkaline solution of a copper salt by oxymethylfurfural. Experiments with 21 samples showed that no genuine honey contained oxymethylfurfural, and that every artificial or mixed honey contained this compound in quantities which, in the latter case, were proportional to the amount of artificial honey present. The iodine and phloroglucide methods together may, therefore, give a reliable indication of the nature of the honey, though the iodine method alone is unreliable (*loc. cit.*), as it is influenced by aromatic substances in the sample.

J. G.

Reducing Powers of Different Sugars for the Ferricyanide Reagent used in the Gasometric Sugar Method. J. A. Hawkins. (*J. Biol. Chem.*, 1929, 84, 79–82.)—The glucose-reducing equivalents of mannose, galactose, fructose, arabinose, xylose, maltose and lactose for potassium ferricyanide have been determined under conditions of the macro blood gasometric method of Van Slyke and Hawkins (*J. Biol. Chem.*, 1928, 79, 739). This method depends upon the quantitative reduction of potassium ferricyanide in an alkaline solution well buffered by a mixture of potassium carbonate and potassium bicarbonate, the excess ferric salt being afterwards measured by the amount of nitrogen gas which it frees from an excess of hydrazine in the Van Slyke–Neill (*J. Biol. Chem.*, 1924, 61, 523) manometric apparatus. The relative reducing values of different sugars vary greatly with the conditions of analysis; consequently, when a new method of sugar determination is introduced, the reduction factors must be ascertained for each individual sugar before it can be determined by the method. A table shows the results. The amount of ferricyanide reduced is directly proportional to the amount of glucose, mannose, maltose, or lactose present; the amount of ferricyanide reduced is directly proportional to the amount of fructose, arabinose, or xylose present when the concentration of these sugars does not exceed 0.1 mgrm. per c.c. in the standard solution. The difference in amount of ferricyanide reduced

per mgrm. of sugar when the concentration of fructose, arabinose, or xylose is 0.2 mgrm. per c.c. is only 5 per cent. less than when the concentration is 0.1 mgrm. or less in the standard solution. It is possible to determine the concentrations of these sugars, when one sugar alone is present in solution, by use of the factors and conditions described for the macro blood gasometric method. P. H. P.

Micro Time Method for the Determination of Reducing Sugars, and its Application to Analysis of Blood and Urine. J. A. Hawkins. (*J. Biol. Chem.*, 1929, 84, 69-77.)—The method of Hawkins and Van Slyke (*J. Biol. Chem.*, 1929, 81, 459), in which sugars are determined by the time they require to reduce a known amount of yellow ferricyanide solution completely to colourless ferrocyanide, has been refined so that 0.2 c.c. of blood suffices for duplicate analyses. In the micro method the reaction is carried out in small test-tubes heated in a porcelain dish, which provides a brilliant white background. The accuracy (± 5 per cent. of the amount determined) and the time required (75 to 300 seconds) are the same as with larger samples and with the previous technique. The number of mgrms. of sugar per 100 c.c. of blood is read from a time curve drawn from the average results obtained from the reduction of ferricyanide by standard glucose solutions under conditions of blood determinations. A diagram shows the comparison of results obtained by the Van Slyke and Hawkins gasometric method with those yielded by the micro blood sugar method, in analyses of 20 bloods, normal and pathological. A procedure is outlined for the application to urine analyses of the same reagents and apparatus used for blood sugar determinations, although such a micro method is not required for urine. The analysis is planned for use with urines, such as those encountered in diabetes, in which the glycosuria is so gross that its significant variations can be satisfactorily shown by measurement of the total reducing substances. The method is accurate to within 0.1 grm. of glucose per 100 c.c. of urine. A curve is given from which the amount of sugar in the urine may be found, and a table shows the comparison of the Van Slyke and Hawkins gasometric and the micro time methods for sugar in diabetic urines.

P. H. P.

Pecan Oil. G. S. Jamieson and S. I. Gertler. (*Oil and Fat Ind.*, 1929, 6, 23-24.)—Oil expressed from pecan nut waste (*Hicoria pecan*) had a mild pleasant flavour and was suitable for salad oil. The nuts contain 60-70 per cent. of oil, but, owing to the value of the nuts for edible purposes, only the waste is available for oil production. The sample examined had the following characteristics:—Sp. gr. at 25°/25°, 0.9141; n_D^{25} , 1.4692; saponification value, 190.0, iodine value (Hanus) 100.0; Reichert-Meissl value, 0.05; Polenske value, 0.30; acid value, 7.0; acetyl value, 7.4; unsaponifiable matter, 0.35 per cent.; saturated acids (corrected), 5.09; unsaturated acids (corrected), 89.54 per cent., of iodine value, 105.5. The composition was as follows:—Oleic acid, 77.8; linolic, 15.8; myristic, trace; palmitic, 3.3; stearic, 1.9; and arachidic acid, 0.1 per cent. D. G. H.

Mlanda Seed and Kullan Nut Oils. (*Bull. Imp. Inst.*, 1929, 27, 281-286.)—The Mlanda plant (*Sesamum angustifolium*, Engl.) from Tanganyika is grown for

its leaves, and yields small oval and mostly dark coloured seeds with pitted seed coats (distinguishing it from commercial sesame seed). The seeds contained 28.9 per cent. (31.2 per cent. on dry seeds) of a pale green limpid oil of sp. gr. at 15°/15° 0.9365; n_D^{20} , 1.4708; saponification value, 181.6; iodine value (Hübl, 17 hours), 117.7; acid value, 16.8; Baudouin's test, positive. The composition of the meal was: Moisture, 7.5; fat, 7.0; crude protein, 22.2; carbohydrates, 17.2; crude fibre, 39.9; and ash, 6.2 per cent. The seed could not compete with ordinary sesame seed chiefly owing to low oil and high fibre content.

Kullan nuts (*Balanites orbicularis*) from British Somaliland, were $\frac{3}{4}$ to $1\frac{1}{2}$ inches long and $\frac{1}{2}$ to $\frac{3}{4}$ inch in diameter, with pale, rough, thin, brittle woody shells, and crinkled yellowish kernels, $\frac{1}{2}$ to $\frac{7}{8}$ inch long and $\frac{3}{8}$ to $\frac{1}{2}$ inch in diameter, containing 37.2 per cent. (39.2 per cent. on dry kernels) of a golden-yellow limpid oil, which had the following constants:—Sp. gr. at 15°/15°, 0.9184; n_D^{20} , 1.4623; saponification value, 192.7; iodine value (Hübl 17 hours), 75.9; acid value, 0.3; unsaponifiable matter 0.5 per cent., and solidifying point of fatty acids, 38.6° C. Saponin was present in the residual meal, which was free from cyanogenetic glucosides, but showed the presence of one or more alkaloidal constituents. The meal contained: Moisture, 9.1; crude proteins, 28.8; oil, 7.0; carbohydrates, 47.4; crude fibre, 3.5; and ash, 4.2 per cent.

D. G. H.

Japanese Ginger. L. Rosenthaler. (*Amer. J. Pharm.*, 1929, 101, 653–654.)—There are 3 grades of ginger in Japan, Kinki, Tuegoku and Shilaku. One-year-old rhizome is used at table with salt, and two-years-old as a remedy and an appetiser. Examination of a sample of Japanese ginger showed that single and grouped starch granules were present, the latter being mostly of equal size. The sizes found were (in mm., with length as numerator and width as denominator) 42/28, 28/24.5, 35/24.5, 45.5/30, 35/26, 44/28, 21/21, 21/14, 26/17.5, 17.5/14, 17.5/15, 16/14, 14/10.5, 17.5/10.5, 21/17.5, 13/10.5. The anatomical structure is similar to that of other sorts of ginger. Large oil cells with yellow content are numerous; no red colour is produced by the vessels or fibres with phloroglucinol hydrochloric acid, and the vessels are frequently associated with tubes of tannin.

D. G. H.

Monosodium Glutamate as a Chemical Condiment. J. E. S. Han. (*Ind. Eng. Chem.*, 1929, 21, 984–987.)—Monosodium glutamate is now used to a large extent, particularly in China, as a condiment. It has a meat-like taste in solution, and the highest flavouring efficiency is obtained when it is used in soup and other dishes containing but little common salt. It is prepared chiefly by the hydrolysis of gluten with hydrochloric acid, crystallisation of the glutamic acid hydrochloride, neutralisation of the latter with sodium carbonate, and removal of the sodium chloride by fractional crystallisation.

W. P. S.

Determination of Aluminium in Plant Materials. O. B. Winter and O. D. Bird. (*J. Amer. Chem. Soc.*, 1929, 51, 2964–2968.)—In determining aluminium in vegetable and animal foods, the samples were prepared as for table use, any impurities not removable in this way being scraped off and the parts

washed. Fresh material was dried at about 35° C., and the dry residue ground to pass a 20-mesh sieve. From 1 to 30 grms. of this material is heated in a platinum dish in an electric muffle to just below redness and left overnight, any unburnt carbon being ignored. The ash is digested with hydrochloric acid and centrifuged, the supernatant liquid being decanted and the residue washed once with about 5 c.c. of water by centrifuging and decanting. The undissolved residue is washed into a platinum crucible with a fine jet of water, the water being evaporated and the dry matter ignited, if necessary, fused with 0.5 gm. each of sodium and potassium carbonates, taken up with hydrochloric acid and added to the original solution. After addition of a few drops of nitric acid, boiling to oxidise the iron, and removal of the silica by dehydration, the solution is transferred to a centrifuge tube of about 25 c.c. capacity with marks at 15, 20, and 25 c.c.. The iron and aluminium are precipitated, and the iron is separated by Myers, Mull, and Morrison's method (ANALYST, 1928, 53, 547); as practically all the materials analysed contain sufficient iron to carry down the aluminium, but not enough phosphoric acid to ensure complete precipitation of the iron and aluminium as phosphates, no iron but about 0.1 gm. of ammonium hydrogen phosphate is added to each sample. The solution is made up to 25 c.c., an aliquot part of this being transferred to a 50 c.c. flask, together with water to 20 c.c., and hydrochloric acid sufficient just to redden added litmus paper. The aluminium is then determined by the colorimetric method described (*J. Amer. Chem. Soc.*, 1929, 51, 2721). The sodium hydroxide used should be prepared from the metal, and a blank test of all the reagents made, the results being corrected accordingly.

All the materials examined contained aluminium, the parts per million of dry substance varying from 2 in wheat flour to 325 in peanut shells. In all cases of unusually high aluminium content (lettuce, carrot tops, beet tops, etc.) the material is such that the adhering impurities could not be removed completely. Specially cleaned apples, red beets, potatoes, and carrots contained respectively 5.2, 5.9, 4.2, and 22.8 parts per million of dry substance.

T. H. P.

Comparative Study of Methyl and Ethyl Protocatechuic Aldehyde.

L. Klotz. (*Amer. J. Pharm.*, 1929, 101, 442-447).—Vanillin and ethyl vanillin were found to exhibit a great similarity in colour reactions, and the following tests for vanillin can also be used for the detection of ethyl vanillin in flavouring extracts:—(1) *Buard's indole reaction* (*Compt. Rend. Biol.*, 1908). To one drop of alcoholic solution of indole in 16 drops of hydrochloric acid is added a 0.02 per cent. alcoholic solution of vanillin or ethyl vanillin, when a rose-red colour is developed. (2) *Lind's test* (*Z. Wiss. Mikroskop.*, 1885, 495): When one drop of a solution containing 1 per cent. of phloroglucinol is added to 2 c.c. of 1 per cent. solutions of vanillin and ethyl vanillin no colour is formed. With 30 drops vanillin gives a reddish-pink, and ethyl vanillin a light pink colour; both become rose-red on heating. (3) *Ferric chloride*: Ferric chloride test solution (U.S.P., X., test for phenolic groups) is added to 2 c.c. of 1 per cent. solutions, when a dark blue colour is formed with vanillin, whilst with ethyl vanillin the colour assumes a greenish tint. (4) *Lead*

acetate: Two c.c. of a 1 per cent. vanillin solution produce a heavy white precipitate with lead acetate solution (U.S.P., X.), whilst ethyl vanillin produces only a white turbidity. (5) *Bohrisch's camphor test*: When 0.5 gm. of camphor is dissolved in hydrochloric acid, and 10 drops of the solution are added to 2 c.c. of a 1 per cent. vanillin solution, a dark-green colour results, whilst with ethyl vanillin the colour is similar, but darker in shade. (6) *Friese's formaldehyde test* (*Sudd. Apoth. Ztg.*, 1907, 752): When 5 c.c. of milk, containing traces of formaldehyde, are shaken with 10 c.c. of hydrochloric acid, and a particle of phloroglucinol and vanillin or ethyl vanillin, there is produced a dark blue coloration which does not differ with either compound. (7) *Allen's test for acetone*: On the addition of vanillin or ethyl vanillin to a mixture of equal parts of hydrochloric acid and sulphuric acid and a liquid containing a trace of acetone, a similar dark blue colour results with either compound. (8) *The thalleioquin test* (Hargreaves, *Amer. Pharm. Assoc. J.*, 1926, 15, 2): Vanillin shows a green coloration, and ethyl vanillin a yellow-green colour when to 2 c.c. of a 1 per cent. solution are added 10 drops of chlorine water and an excess of 10 per cent. ammonium hydroxide; with bromine water instead of chlorine water, vanillin gives a deep yellow-brown colour, and ethyl vanillin an orange colour. (9) *Jolles' test for pentosans*: Both vanillin and ethyl vanillin give a red coloration in the cold with the osazone of laevulose, in presence of hydrochloric acid. (10) *Grofe's test for wood fibre* (*Oesterreich. Botan. Z.*, 1905): Wood fibre moistened with vanillin or ethyl vanillin in solution in iso-butyl alcohol and with sulphuric acid gives a blue to blue-green coloration with vanillin, and a similar, though a yellower green coloration with ethyl vanillin. (11) *Raikow's test for chlorine* (*Chem. Ztg.*, 22, 20): If a solution containing 1 gm. of vanillin or ethyl vanillin is evaporated to dryness, and the residue placed upon benzoic acid which is being heated, a red colour develops in the residue if chlorine is present; the colour obtained with vanillin is rather more pronounced than that given by ethyl vanillin. The reactions are due either to the hydroxy or aldehyde groups, and substituted groups have little or no effect on the colours. Other compounds containing hydroxy or aldehyde groups in the proper position (e.g. *p*-hydroxy-benzaldehyde) give similar results.

D. G. H.

Two South American Cinchona Barks. L. Rosenthaler. (*Amer. J. Pharm.*, 1929, 101, 651-652.)—*Castrona bark* consists of flat forms and half tubes, approximately 50 cm. long, 5 cm. broad, and 0.65 cm. thick, with outer and inner surfaces (where not covered with cork or outer bark cells), reddish-brown and, in spots, bright red. In flat forms the outer surface shows irregular longitudinal furrows, and the inner numerous parallel furrows, and in half-tube forms coarse cross-hatchings are present. On heating, white, followed by reddish-brown vapours may appear, and finally some brown-purple tar forms. Latex vessels are absent in cross section, but much sclerotic tissue is present; bast fibres in radiate groups are mostly 790-900 μ long. The total alkaloid content was 3 per cent.

Naradjada bark: The flat forms and half tubes, up to 45 cm. long, 4.5 cm. wide, and 0.8 cm. thick, have mostly smooth outer surfaces, broken in places by shallow

or deep depressions. Fracture in the outer layers is smooth and in the inner fibrous. On heating, white, then slightly red vapours are produced, followed by the formation of a brownish tar. No latex vessels are present. The outer portion is sclerotised, and some stony structure is also present in the inner portion. In addition to normal bast fibres, there are other unusually long ones, and in the radial direction the bast fibres are discontinuous, but in tangential section are in well-marked rows. The longest bast fibre noted was $1275\ \mu$, but they were often from 900 to $1200\ \mu$. Oxalates are present, particularly in the medullary rays, starch granules are few, either single or grouped up to 5. The total alkaloid content was 2.0 per cent.; the general structure is of the *Pubescens* type.

D. G. H.

Determination of "Free Nicotine" in Tobacco. Apparent Dissociation Constants of Nicotine. H. B. Vickery and G. W. Pucher. (*J. Biol. Chem.*, 1929, **84**, 233-241.)—When samples of tobacco are subjected to steam distillation without the addition of alkali, a part of the nicotine usually passes over into the distillate; it has been noted that the relative magnitude of this part varies with the hydrogen ion concentration of the extract. The determination of the "free nicotine," as this volatile part of the nicotine has been called, is of some importance in the chemical examination of tobacco, since the harsh flavour of certain tobaccos has been attributed to a high proportion of this component. Free nicotine is present in tobacco because of the hydrolysis of the nicotine salts in the tissue. The proportion present at ordinary temperatures may, therefore, be read directly from the dissociation curve of nicotine at the point corresponding to the reaction of the sample. Nicotine is a di-acid base, and its apparent dissociation constants were determined by Kolthoff (*Biochem. Z.*, 1925, **162**, 389). Since he used a somewhat impure preparation of the substance and determined only three or four points on each limb of the curve by a colorimetric method, it was thought desirable to repeat the determination. A highly purified nicotine has been prepared, and its dissociation constants have been determined by the electrometric method, and a dissociation curve is given from which the proportion of the total nicotine occurring in the free form in a tobacco extract of known hydrogen ion concentration may be read. A table shows the proportion of free nicotine in various samples of tobacco. The curve from which the amounts of free nicotine are read applies only to the temperature at which the dissociation constants were determined, and the nicotine values represent the proportions free at this temperature. Therefore there is no reason to suppose that the magnitude of the results should duplicate those secured from the same samples by distillation with steam, which are also given. It is suggested that this method for the determination of the free nicotine of tobacco is simpler and more precise than that hitherto employed, and should prove equally useful in forming a judgment of the quality of tobacco.

P. H. P.

Pyrethrum Flowers. I. Determination of the Active Principles. C. B. Gnadinger and C. S. Corl. (*J. Amer. Chem. Soc.*, 1929, **51**, 3054-3064.)—Both pyrethrin I and pyrethrin II reduce alkaline copper solutions and may be determined by Folin's method for sugar in blood (*ANALYST*, 1920, **45**, 227; 1922,

47, 268). Among the reagents used are: Petroleum spirit, 90-99 per cent. distilling between 20° and 40° C., max. b. pt. 60° C.; a solution of 20 grms. of Horne's basic lead acetate in recently boiled water to 1 litre; alkaline copper solution, prepared by dissolving (1) 2.5 grms. of pure copper sulphate in about 100 c.c. of warm water, and (2) 5 grms. of sodium potassium tartrate and 7.5 grms. of sodium hydroxide in 100 c.c. of cold water, transferring the cold solutions to a 500 c.c. flask and making up to volume—this solution should not be used when more than 3 days old; a solution containing 1 gm. of anhydrous dextrose and 40 c.c. of aldehyde-free alcohol per 200 c.c., which keeps for months; a solution obtained by diluting 10 c.c. of the previous solution and 210 c.c. of aldehyde-free ammonia to 250 c.c.—this solution should be made fresh each week. Use is made of Folin sugar tubes, blown to contain 15.5 c.c. to the base of the constriction, the bore of which should be the same for all tubes in a set; when heated to 78° C., the surface of the liquid must lie within the constricted length.

To determine pyrethrin in pyrethrum flowers, 20 grms. of the ground (about 30-mesh) flowers are extracted for 5 hours with the petroleum spirit in a Soxhlet extractor, the solution being then cooled to about 20° C., left for at least 30 mins., and filtered into a 400 c.c. beaker. After addition of a few grains of ignited sand, the solvent is expelled at a temperature not exceeding 75° C., the residue being at once transferred to a 100 c.c. flask by means of five or six portions of boiling 95 per cent. aldehyde-free alcohol, sufficient of which is used to make the volume 80-85 c.c. The hot solution is treated with 15 c.c. of the basic lead acetate solution, made up to the mark with hot alcohol, well shaken, cooled at once to 20° C., and again made up to the mark with alcohol. After filtration the liquid is treated with about 1 gm. of anhydrous sodium carbonate, shaken frequently during 10 or 15 minutes, and filtered, 10 c.c. of the clear filtrate being immediately pipetted into a Folin tube and there mixed, within the bulb, with 6 c.c. of the alkaline copper solution. Into a second tube, 10 c.c. of standard dextrose solution and 6 c.c. of alkaline copper solution are pipetted. The two tubes are left upright in a bath at $78 \pm 0.2^\circ$ C. for 45 minutes, and then in water at 20° C. for 3 minutes. Each is then treated with 10 c.c. of Folin's reagent, left for 3 minutes, stoppered and mixed, the contents being transferred to a 100 c.c. flask, made up to volume, and, with the first tube only, filtered through a thick asbestos pad in a Gooch crucible, using gentle suction. The solutions are then compared in a Duboscq or Klett colorimeter and the dextrose equivalent to the unknown solution is calculated in the usual way. The corresponding amount of pyrethrin I or of a 50:50 mixture of pyrethrins I and II is read off from the following table, the figures in which represent milligrams.

D.	PI.	PI+II.	D.	PI.	PI+II.	D.	PI.	PI+II.
0.8	5.14	5.48	1.5	9.23	9.85	2.2	14.31	15.26
0.9	5.69	6.07	1.6	9.88	10.54	2.3	15.17	16.18
1.0	6.24	6.66	1.7	10.55	11.25	2.4	16.09	17.16
1.1	6.81	7.26	1.8	11.24	11.99	2.5	17.05	18.19
1.2	7.39	7.88	1.9	11.96	12.76	2.6	18.11	19.32
1.3	7.99	8.52	2.0	12.71	13.56	2.7	19.25	20.53
1.4	8.60	9.17	2.1	13.49	14.39	2.8	20.55	21.92

Blank determinations are advisable. If the blank result lies between 0.05 and 0.1 mgrm. of dextrose, it may be neglected, but reagents giving a higher blank should be discarded. In a number of samples of pyrethrum flowers, the pyrethrin content varied from 0.4 to 1.2 per cent., the stems containing only about 0.04 per cent. The active principles are the same in Japanese as in Dalmatian flowers. With pyrethrin I, a 1:80,000 aqueous solution containing less than 0.5 per cent. of alcohol is fatal to 100 per cent. of cockroaches within 24 hours, the corresponding dilution for pyrethrin II being 1:75,000. T. H. P.

Monobromoguaiacol Carbonate. Determination of Guaiacol Carbonate. L. H. Chernoff. (*J. Amer. Chem. Soc.*, 1929, 51, 3072-3074.)—Addition of bromine to a methyl alcoholic solution of guaiacol carbonate results in the separation of bromoguaiacol carbonate in acicular crystals, m.pt. 178° C. The formation of this compound serves for the determination of guaiacol carbonate: 0.1-0.5 grm. of the carbonate is heated in a steam-bath in a 100 c.c. Erlenmeyer flask with 10-20 c.c. of methyl alcohol until dissolved. The hot liquid, removed from the bath, is treated with about 1 c.c. of bromine, and left, with occasional shaking to promote crystallisation, for 10 minutes; an equal volume of water is then added and the whole left for a further period of 10 minutes, after which it is filtered through asbestos in a weighed Gooch crucible. The precipitate is washed with 50 per cent. methyl alcohol solution, dried for about an hour at boiling water temperature, and weighed. Multiplication of the weight of the bromine derivative by 0.6343 gives the weight of guaiacol carbonate.

In mixtures with the usual excipients, such as starch, sugar, gum acacia and gum tragacanth, a preliminary separation by means of a solvent like chloroform, in which the carbonate dissolves readily, is advisable. From 0.5 to 0.1 grm. of the powdered material is heated to boiling with 10 c.c. of chloroform and filtered into an evaporating dish, the undissolved residue being well washed with chloroform. After elimination of the solvent on a steam-bath, the residue is dissolved in hot methyl alcohol and brominated as above. T. H. P.

Purification and Preservation of Ether for Anaesthetic Use. S. Palkin and H. R. Watkins. (*Ind. Eng. Chem.*, 1929, 21, 863-867.)—Ether containing peroxide and aldehydes may be purified by distillation over pyrogallol or permanganate and then passing the distillate through a strongly alkaline solution of either of these reagents. The purified ether may be preserved for more than one year by placing in the container a small quantity of asbestos impregnated with strongly alkaline pyrogallol or permanganate solution. When required for use, the ether may be poured off without resorting to filtration. W. P. S.

Determination of Nitrates in Bismuth Carbonate. G. J. W. Ferrey. (*Quarterly J. Pharm.*, 1929, 2, 205-216.)—The official method of the Fertiliser and Feeding Stuffs Act, 1926, modified by the use of methyl red as indicator, gave a maximum error of 1.1 per cent. when 5 grms. of sample were taken, and is preferable to the use of Devarda's alloy (McLachlan, *ANALYST*, 1921, 46, 383). Seven

possible sources of error in the phenoldisulphonic acid (B.P.) method were also examined, and the conclusion reached that the maximum error need not exceed 5 to 7 per cent., the principal disturbing factor being the quality of the light when the ammoniacal solutions are being matched. The method may fail, however, when the samples under examination differ greatly from the B.P. standard. In the indigo-carmin method (Simmons, *ANALYST*, 1908, 33, 440) the 25 c.c. of sulphuric acid should be added in two equal portions, and the titration time should not exceed 40 seconds. The standard indigo-carmin and potassium nitrate solutions are stable for at least 2 months. If 0.5 grm. of carbonate is taken, the method is reliable for the determinations of 4 per cent. or less of subnitrate.

J. G.

Luminescence of Creatinine. G. Reif. (*Z. Unters. Lebensm.*, 1929, 58, 28–32.)—Solutions of creatinine in a fatty acid (*e.g.* butyric acid) prepared at 100° C., show the same blue luminescence as solid creatinine in the light of the quartz lamp, which changes, however, to yellow-green if the solution is heated at 165° to 170° C. for 10 minutes. The crystals which separate from the cool solution may be recrystallised from alcohol, and are soluble in water and glacial acetic acid, but not in organic solvents. Analysis by combustion showed that they have the same composition as creatinine, and the change is probably tautomeric and involves the production of an enolic form (with a double-bond) from a ketonic form. The colour returns to blue in the presence of 0.1 *N* acid, but is regenerated by alkali. It is not produced with inorganic acids or non-fatty organic acids, while the numerous other amines tested in the same way gave either no colour, or else a blue colour only. The influence on the examination of foodstuffs containing both creatinine and fatty acids is indicated.

J. G.

Biochemical.

Silicosis in Industry in Britain. E. L. Middleton. **Biophysics of Silica and the Etiology of Silicosis.** P. Heffernan. (*Brit. Med. J.*, 1929, Sept. 14, 485–492.)—Silicosis is treated from the point of view of the etiology, pathology, symptomatology, diagnosis, prognosis, nomenclature, and industries concerned. Since only particles in a very fine state of division reach the ultimate pulmonary tissue, the visual appearance of an atmosphere is no criterion of its freedom from danger. In sections of silicotic lung, the average size of the particle is about 1 μ . Silica is a normal constituent of both plant and animal cells. Silicosis is regarded as the result of local action of hydrated silica on the pulmonary tissue, the action being of a physico-chemical nature, and the speed of development depending (other things being equal) on the rate of formation of fresh silica hydrosol, and its contact with pulmonary tissue, so that the addition of alkalis (which favour the formation of silica hydrosol from silica) to silica dust, accelerates the development of silicosis. A combination of alkali and silica, such as that found in siliceous scouring powders, only requires wetting for the immediate production of active silica hydrosol, and a variable system of sodium oxide, silica and water,

with the silica in the hydrosol state, is set up. When quartz particles alone enter the lung, hydration is only brought about slowly by the very faintly alkaline tissue juices. These facts explain the very varying times shown in different industries of the appearance of symptoms of silicosis. This slow hydration has been paralleled with Ringer's fluid; asbestiosis is regarded as a true silicosis, and the characteristic "club moss" growths in lungs affected by asbestiosis are regarded as osmotic silica products.

D. G. H.

Some Physiological Aspects of Copper in the Organism. F. B. Flinn and J. M. Inouye. (*J. Biol. Chem.*, 1929, 84, 101-114.)—There is increasing evidence that, up to a certain point, copper may be beneficial to both animals and plants, but that, in excess of this quantity, ill effects sometimes, but not always, ensue. A discussion is given of previous work by various investigators. Protein affects the toxicity of copper; 0.2 gm. of a mucin-like material excreted by cryptobranchs will remove 10.8 mgrms. of copper from a solution containing 75 mgrms. of copper per litre. Copper is shown to have a close affinity for all proteins, and the protective action of food in this connection is mentioned. Some of the physiological effects of copper have now been studied because of the suggestion of Mallory (*Amer. J. Path.*, 1925, 1, 117) that haemochromatosis may result from the continuous ingestion of small amounts of this metal. The excretion rate and the distribution of the metal in the bodies of animals subjected to known amounts of copper have been determined. The largest amount was recovered from the faeces, a good proportion from the oesophageal tubes, and small proportions from the urines and tissues. A table shows the distribution of copper in the bodies of rats which were given 2 mgrms. of copper per day in their drinking water for 12 months; the liver is the chief depository for the metal. Another table gives the copper content of the livers of various animals with no known copper exposure. Copper is found in the hair, and a very small amount in the bones. The action of bone on metals in solution as chlorides is shown, and the distribution of copper in blood. Copper is found in normal blood. Its average distribution in the blood of 4 dogs which were being given each day 300 mgrms. of very fine copper in capsules, was 2.97 mgrms. per 100 grms. of plasma, and 1.27 mgrms. per 100 grms. of corpuscles. An examination of thirty-three normal human livers showed a copper content of from 2.4 to 15 mgrms. per 100 grms. of tissue. The livers of 1 day old animals often contain as much copper as those of their parents. The evidence from a study of the blood changes occurring in the living animal receiving copper, with reference to the possible formation of methaemoglobin, tends to show that the copper in the blood is in some combination which is acted upon by the hydro-sulphite used in the Van-Slyke and Neil method for reducing methaemoglobin to haemoglobin, and that this combination reacts differently from the compounds which aluminium and lead form in the blood, or from the haemocyanin of lobster blood. There is no evidence that copper ingested by the body in the normal way acts as a haemolytic agent. No increase in the storage of copper in the liver was found, except in cases where the animals were given far larger amounts of copper per

kilo. of body weight than man would normally be exposed to in his daily or industrial life. The work indicates that copper may play some important rôle in stimulating blood formation, and that its constant presence in the liver, even in the liver of the foetus, may not be due merely to the fact that this organ has among its functions that of being a filter. The combination in which it is held cannot be judged at this stage, but it must exert an important influence on the haematopoietic system and on the metabolism of the body as a whole. An examination of the blood of guinea pigs and dogs showed that the oxygen-carrying capacity of the blood was increased when copper was being given to the animals.

P. H. P.

Electrolytic Method for the Determination of Small Amounts of Mercury in Body Fluids and Tissues. A. G. Young and F. H. L. Taylor. (*J. Biol. Chem.*, 1929, 84, 377-391.)—Mercury determinations in physiological fluids require: (1) An adequate method of digestion, (2) an efficient method of concentration, and (3) an accurate method of determination free from complications by interfering agents. Data are presented which indicate: (1) Hydrolytic oxy compounds of mercury are not formed in the presence of sulphuric acid. (2) Reduction of the mercury to the low valence form increases its loss in open digestion. (3) Mercury is not precipitated completely on copper, even after digestion and prolonged standing (but *cf.* Evans and Clarke, *ANALYST*, 1926, 51, 224). A method for the determination of mercury is therefore described, which is fairly rapid and accurate for determinations of mercury in physiological fluids, and data showing its accuracy are presented. The upper limit of accuracy is within 1 per cent. of the true value, which compares favourably with other biological methods. An electrolytic method for concentration is combined with a titration method for determination, and obviates difficulties from the presence of interfering agents, or the necessity for expensive apparatus. The method has been used for 400 determinations on physiological fluids without complications, and from these it has been possible to make complete studies of the excretion and distribution of mercury on patients and animals. The wiring diagram for the electrolysis is given, and also a diagram of the electrodes devised. Since the mercury in the electrodes is enclosed it cannot spill into the solutions. The platinum foil for the deposition of mercury is about 1 sq. cm. in size. The electrode vessels are placed under a wooden rack from which the lower shelf has been removed, and the electrodes are then inserted from above, the rubber stoppers fitting the holes and keeping the set rigid. With a potential difference of 6 volts, and a current of 0.5 ampere the deposition is complete overnight. Halogens present during electrolysis do not affect the yield. The procedure for urine is as follows:—In an 800 c.c. Kjeldahl flask 250 c.c. of urine are placed, and diluted with 100 c.c. of water; 2 c.c. of concentrated sulphuric acid and 25 c.c. of nitric acid are added, and the contents mixed, the internal condenser as used by Booth Schreiber and Zwick (*J. Amer. Chem. Soc.*, 1926, 48, 1815) being kept in place. Then 2 grms. of potassium permanganate are added, together with 10 c.c. of chloroform (this latter to prevent foaming), and digestion is continued with the condenser in place until odour and colour disappear. More

permanganate may be added from time to time as required. When digestion is complete the liquid is transferred to the electrolysing vessel, and the current is allowed to run overnight. If the ammeter shows a lower current than 0.5 amp., it is adjusted by addition of nitric acid, drop by drop, to the electrode vessel. After the deposition of the mercury the electrode is washed with distilled water, and then the deposit is dissolved in hot fuming nitric acid (5 c.c.) contained in the titrating vessel, the electrode is again washed, and the washings added to the mercury solution. The volume is made up to 100 c.c. with distilled water, one drop of potassium permanganate is added to oxidise any possible mercurous compounds formed, the contents are cooled, and 3 per cent. hydrogen peroxide is added, drop by drop, to remove the permanganate colour. Five c.c. of 10 per cent. ferric ammonium alum (chloride-free) are added, and the solution is titrated with 0.05 or 0.01 *N* potassium thiocyanate solution with a Folin-Wu micro sugar burette. Titration is continued until the first rose tint appears. After removal of the deposited mercury all reagents must be chloride-free. Blank determinations should be made, and the results subtracted from the total titration value. No digestion is required in the case of spinal fluids. The method can also be applied to mercury determinations in tissues and faeces.

P. H. P.

The Potato as an Index of Iodine Distribution. R. E. Remington, F. B. Culp and H. von Kolnitz. (*J. Amer. Chem. Soc.*, 1929, 51, 2942-2947.)—The average iodine contents (in parts per billion (1000 millions) of dry matter) of Irish potatoes grown in various districts are: South Carolina, 211; Maine, 195; Idaho, 110; Michigan, 94; Minnesota, 86. Large variations occur in different samples from the same area and from soils of identical type. The iodine content of the potatoes increases progressively from the sea to the Appalachian, the relative amount of clay in the soil increasing similarly. It is suggested that the principal source of the iodine is disintegrated granite rocks, supplemented by mixed commercial fertilisers. The immediate influence of the sea on the iodine content is not seen beyond a very narrow belt along the coast. In determining the iodine, the organic matter was destroyed by simple ignition of the material in a porcelain dish at a temperature not exceeding 450°, organic as well as inorganic iodine being retained by the ash under such conditions.

T. H. P.

Gasometric Determination of Methaemoglobin. D. D. Van Slyke and A. Hiller. (*J. Biol. Chem.*, 1929, 84, 205-210.)—The method of Van Slyke (*J. Biol. Chem.*, 1925, 66, 409) for methaemoglobin determination has been simplified by the adaptation to it of the carbon monoxide-binding capacity technique of the authors (*J. Biol. Chem.*, 1928, 78, 807). The principle, as before, is that introduced by Nicloux and Fontes (*Bull. Soc. chim. biol.*, 1924, 728; *ANALYST*, 1924, 49, 392). Two determinations are required. In one (A) the normal or active form of haemoglobin, capable of binding oxygen and carbon monoxide, is determined by measuring the carbon monoxide-binding capacity of the haemoglobin-methaemoglobin mixture. In the other (B) sodium hydrosulphite is added,

changing methaemoglobin into active reduced haemoglobin, and the total haemoglobin is determined by the carbon monoxide-binding capacity. The difference, B-A, indicates the methaemoglobin. The technique introduced has the advantage that all the operations, reduction with hydrosulphite, saturation with carbon monoxide, and determination of carbon monoxide bound by haemoglobin, are carried out in the chamber of the Van Slyke-Neill apparatus. Consequently, the procedure is simpler, more rapid, and requires much less blood, as little as 0.2 c.c., or even 0.1 c.c., sufficing for an analysis. In a determination of the carbon monoxide capacity in blood reduced by hydrosulphite, the presence of hydrosulphite and ammonia appears to lower somewhat the affinity of reduced haemoglobin for carbon monoxide, so that 100 mm. tension of the latter, instead of only 30, are required to insure complete conversion of the haemoglobin to carboxyhaemoglobin. A table shows the results obtained with amounts of blood varying from 2 c.c. to 0.1 c.c. The procedure is described in detail. P. H. P.

Reaction of Azine Compounds with Proteolytic Enzymes. G. M. Richardson and R. K. Cannan. (*Biochem. J.*, 1929, 23, 624-632.)—A number of workers have reported that precipitates are formed when various azine dyes are added to solutions of proteolytic enzymes, and that, in some cases, the mother liquors have lost their protease activity, which has, in part, been transferred to the precipitates. Marston (*Biochem. J.*, 1923, 17, 851) found that safranine was a specific precipitant for all the protease activities he tested, *viz.* pepsin, trypsin, erepsin, yeast protease and papain, but that it did not remove other non-proteolytic enzymes from solution. Other azonium salts, azines and eurhodines behaved similarly towards trypsin, and Marston concluded that he was observing a specific interaction between the azine nucleus and the structure peculiar to a protease, and drew an analogy between the azine ring as represented by the various dyes used and the piperazine ring which he believes to be a dominant feature of the protein molecule. This argument has recently been used to support the diketopiperazine structure of protein. The authors have now examined the kinetics of protease activity by a quantitative study of the anticatalytic effect of azine compounds on the activity of the protease; they hoped at the same time to assemble data which would permit the precise use of this reaction as an economical means of purifying protease preparations. The results confirm the observation of Marston and others that the addition of safranine or neutral red to a solution of pepsin or trypsin leads to the separation of a flocculent precipitate. In the case of pepsin solutions, including gastric juice itself, the precipitate removed the peptic activity from solution; on the other hand, the supernatant liquors from the trypsin precipitates, lost no significant proportion of their activity. The optimum conditions of concentration and P_H for the complete removal of pepsin from solution by this means have been determined, and a method is described for the recovery of the precipitated pepsin. The minimum efficient concentration of dye was found to be 0.1 per cent., and the optimum P_H for purification just above 3. Azine dyes do not "poison" the catalytic activity of either pepsin or trypsin; thus there-

exists in solution under the experimental conditions no significant concentration of a specific protease-azine complex antagonistic to protein hydrolysis. Therefore no support is given by these results to the view of Marston that the azine nucleus reacts specifically with a protease with the formation of a protease-azine complex, and the formation of precipitates when azine dyes are added to protease preparations may not be used as an argument either for the piperazine structure of proteins or for any structural scheme of the mechanism of protease digestion. P. H. P.

Nephelometric Determination of Pepsin. C. G. Van Arkel. (*Pharm. Weekblad*, 1929, **66**, 857-864.)—Pepsin may be determined by physical methods (e.g. from the changes in viscosity, electrical conductivity and refractive index of the mixture of enzyme and substrate); or chemically, from the decrease in the amount of substrate, or the increase in the amount of reaction products. The method proposed is based on that of Kleinmann (*Klin. Woch.*, 1924, **14**, 572), and depends on the comparison of the turbidity produced from a 20 per cent. solution of sulpho-salicylic acid and the undigested substrate with that from a standard solution of albumin. The P_H value of 40 c.c. of a dilute serum solution (1:30) is adjusted (*vide infra*), by addition of 2 to 20 c.c. of *N* hydrochloric acid, and the volume diluted to 150 c.c. with physiological salt solution and maintained at 40° C. The pepsin solution (50 c.c. containing 100 mgrms.) is then added at 40° C., and the reaction is stopped at 5 minute intervals by pipetting 5 c.c. into 10 c.c. of 4 *N* sodium hydroxide solution. The nephelometric measurement is made 3 minutes after the addition of 5 c.c. of 25 per cent. hydrochloric acid and 8 c.c. of reagent, and a blank experiment, in which the pepsin is omitted, must be carried out. It was shown that each pepsin solution has its own optimum P_H value between 1.3 and 2.7 (1.5 to 2.7, 1.5 and 2.0 in the cases tested), and that the P_H value depends to a slight extent on the strength of the solution. The P_H value of the mixture of enzyme and substrate, however, may fall outside the optimum range. In all cases the rate of reaction is almost zero after 35 minutes, when 80 per cent. of the protein is decomposed. J. G.

Action of Papain on the Polarisation of Gelatin. Measurement of Proteolytic Activity. H. C. Gore. (*Ind. Eng. Chem. Anal. Edit.*, 1929, **1**, 203-205.)—The destruction of the first 40 per cent. of the mutarotation of gelatin by papain, as measured by the fall in polarisation at 20° C., is a linear function of the amount of enzyme. A method of measurement of the activity of papain is, therefore, proposed, in which 50 c.c. of a clear 2 per cent. solution of commercial food gelatin, adjusted to P_H 4.8 by addition of 10 c.c. of a Walpole buffer solution, are mixed with 40 c.c. of an aqueous solution or suspension of papain at 45° C. After 1 hour, or longer (in which case a drop of toluene should be added), the mixture is cooled rapidly, and maintained at 5° C. for 16 hours, then warmed at 20° C. for 1 hour, and the rotation measured. Similar readings are obtained for the papain solution alone and for the gelatin solution in the absence of papain, and the proteolytic activity (*P*) calculated from the expression W/wt where *t* is the time in

hours required by w grms. of papain to digest W grms. of air-dry gelatin. W should not exceed 40 per cent., and w is chosen accordingly. For 5 samples of papain P varied from 32 to 65.
J. G.

Observations on the Assay of Vitamin A. J. C. Drummond and R. A. Morton. (*Biochem. J.*, 1929, 23, 785-802.)—The biological method of assay of vitamin *A* is subject to error on the ground of the wide variations that may be encountered, and the necessity of using large groups of animals for each test makes it a costly and laborious matter when many samples have to be examined. It is still uncertain, however, whether the colour reaction of Rosenheim and Drummond, on which an alternative method of determination is based, is due specifically to the vitamin. The authors decided to make a severe comparative examination of the two methods before finally accepting or rejecting the colorimetric method as a routine test, and to extend the comparison to cover a method based on the quantitative examination of the absorption band in the ultra-violet spectrum extending from 280 to 360 $\mu\mu$ (maximum near 328 $\mu\mu$), believed by Morton and Heilbron (*Biochem. J.*, 1928, 22, 987; *ANALYST*, 1928, 53, 503, 664) to be characteristic of vitamin *A*. Six samples of cod-liver oil were selected at random from recently collected materials and examined by the three methods. For the biological tests the "curative" or "recovery" method was used. (The investigation was well advanced before Hume and Smith (*Biochem. J.*, 1928, 22, 504) pointed out the disadvantages of this method, and advised dispensing with the depletion period.) Colorimetric determinations were made by means of a Lovibond tintometer, and also by a spectrophotometer. These two modifications of the test gave very satisfactory agreement. The relative intensities at 328 $\mu\mu$ of the absorption band of the cod-liver oils were measured by the photographic technique. By the biological method, in spite of the use of much larger groups of rats (7-12) for each dose than are usually employed, the individual responses of the animals showed such wide variations as to make it a very difficult matter to detect quantitative differences of less than 100 per cent. in the vitamin *A* potency of cod-liver oils. As far as the relative values of the six oils could be determined by the biological test, they were in agreement with the response to the colour reaction, and with the relative intensities of the absorption band (328 $\mu\mu$). There was very close agreement between the results of the colorimetric and spectrographic methods. A comparison of the biological assay with the two physical methods was also made in the case of a number of other oils, and general agreement between the results found; for these the biological tests were not made quite so thoroughly. Tests were carried out on the six cod-liver oils after they had been stored for a year both in the light and in the dark. In view of the statement of other investigators that certain oils (fish-body oils) may be rich in vitamin *A* without showing the colour reaction, it still seems undesirable to claim that the colorimetric method can generally replace the tedious and inaccurate biological tests. Actually, in a wide experience, no single instance has been found in which there was disagreement between the animal tests and the intensity of the blue colour showing

maximum absorption near 608μ . So far as cod-liver oils are concerned, the authors have no hesitation in recommending the colorimetric and spectrographic methods (taken together) as giving rapid and reliable quantitative results. P. H. P.

Relation of Vitamin A Content to Size of Leaves. L. McLaughlin. (*J. Biol. Chem.*, 1929, **84**, 249-256.)—Vitamin A is very unequally distributed in the parts of a plant but the leaves contain a large fraction of it; probably it is formed in the leaves and then carried to other tissues. The relative vitamin A content of New Zealand spinach leaves of three different sizes has been determined by a rat-growth method. New Zealand spinach plants were chosen for examination because on the same plant may often be found leaves of any size, from those just forming up to others having an upper surface area of 10 to 12 square inches. An attempt was made with each size of leaf to find the quantity of New Zealand spinach which, when supplementing a diet adequate in all respects except vitamin A, would promote an increase in weight of 25 grms. in rats whose body stores of vitamin A had been depleted. The results show that the potency of small leaves is greater than that of large leaves. With small leaves somewhat less than 90 mgrms. and more than 70 mgrms. per week was required; with medium leaves about 90 mgrms. were necessary; and with large leaves more than 110 mgrms. and less than 120 mgrms. was effective in promoting the desired increase in weight. The experimental period was eight weeks. Charts and tables show the results. The weights and the corresponding surface areas of leaves of three sizes were compared, and the ratio of the thicknesses of the three was calculated. The ratio of the thicknesses is approximately the reverse of the ratio of the leaf potencies, indicating, therefore, that the vitamin A content of leaves depends upon the surface area. P. H. P.

Absorption Spectrum of Vitamin A. O. Rosenheim and T. A. Webster. (*Biochem. J.*, 1929, **23**, 633.)—It has been claimed repeatedly that vitamin A is characterised by a selective absorption in the ultra-violet region at about $320\text{--}328\mu$. The authors have subjected this claim to the experimental test. Dehydroergosterol, a sterol with four double bonds, has been prepared from ergosterol as described by Windaus and Linsert (*Liebig's Ann.*, 1928, **465**, 148), and shown by a photographic method to possess an intense absorption exactly in the same region as that claimed for vitamin A. The absorption curve agrees with that obtained by a photo-electric method by Windaus and Linsert. The free sterol, its acetate and the peroxide were each proved, by means of biological tests on rats, to be devoid of growth-promoting properties. The fact that these substances also fail to give a blue colour with arsenic trichloride (or antimony trichloride) is significant, in view of the assumed association of this colour reaction with vitamin A. It would seem, therefore, that selective ultra-violet absorption at $320\text{--}328\mu$, at any rate by itself, cannot be taken as a criterion of vitamin A. P. H. P.

Alleged Relation of Carotin to Vitamin A. W. Dullere, R. A. Morton and J. C. Drummond. (*J. Soc. Chem. Ind.*, 1929, **48**, 316-321T.)—Pure carotin was prepared from the crude material by recrystallisation from hexane in an

atmosphere of nitrogen. After about four recrystallisations the properties of the carotin changed, and it became relatively insoluble and of a more intense colour. The m.pt. rose on recrystallisation from about 170° to 185° C., at which it remained constant. Feeding tests of the "curative" type required very large doses (0.5 mgrm.) to bring about any stimulation of growth, for the activity of the carotin diminishes with purification, and the pure product is regarded as of negligible vitamin A potency. The growth-promoting action of liver oils is not due to carotin. No reason is found for associating the vitamin A of liver fats with dihydro- α -crocetin, nor can it be affirmed or denied that the potency of certain carotinoids is due to a substance or substances differing from the classical vitamin A. Results indicate that the classical vitamin A must be a colourless substance, and its intrinsic potency very much higher than that of any sample of carotin or dihydro- α -crocetin for which data have been published. The carotin and antimony trichloride blue and the vitamin A and antimony trichloride blue resemble each other, but measurement of the absorption bands shows clearly that they are not identical.

D. G. H.

Vitamin A and Carotene. I. Association of Vitamin A Activity with Carotene in the Carrot Root. T. Moore. (*Biochem. J.*, 1929, 23, 803-811.)—Previous work on the possibility of a relationship between vitamin A activity and carotenoid pigmentation is discussed. The question was re-opened by the work of Euler, Euler and Hellstrom (*Biochem. Z.*, 1928, 203, 370). These workers pointed out that in previous biological tests of carotene no provision was made for the presence of vitamin D in the diet, and that the results obtained cannot, therefore, have been reliable. Preliminary experiments in confirmation of the activity of carotene have been described by Moore (*Lancet*, 1929, i, 499). Tests are now described on young albino rats receiving a basal diet adequate in vitamins B and D. Under the experimental conditions specified, fresh carrot root was found to be a much richer source of vitamin A activity than hitherto supposed. Daily doses of 100 mgrms. of the fresh root sufficed to cure xerophthalmia and restore good growth in the rats deprived of vitamin A. Under similar conditions a sample of carrot fat, from which much of the carotene had been removed, was found to be active in a dose of 0.4 mgrm. daily. Carotene (m.pt. 174° C. in air) was found, even after many recrystallisations, to be active in doses of 0.01 mgrm. This agrees with the conclusion of Collison, Hume, Smedley-MacLean and Smith (*Chem. Ind.*, 1929, 48, 631) that carotene isolated from cabbage fat also possesses intense vitamin A activity. A possible explanation is given of the divergent results of other workers. The suggestion of Dulière, Morton and Drummond (*Chem. Ind.*, 1929, 48, 518), that pure carotene is inactive, and that the activity reported by Euler, Euler and Hellstrom may have been due merely to contaminating traces of vitamin A, is improbable for the following reasons:—(1) Carotene samples of a high degree of purity were found invariably to be active. (2) The activity of the carrot fat from which the carotene was crystallised was inferior to that of the isolated pigment. The activity of the pigment, therefore, could not have been

due to the presence of fat carried down as an impurity. (3) Both carotene and carrot fat produce with antimony trichloride a blue coloration which is characterised by an absorption band at $590\mu\mu$. If the physiological activity of these sources is attributable to the same vitamin *A* as contained in cod-liver oil, intense absorption would be anticipated at $610\mu\mu$, but no band was visible in this position. There can be no doubt as to the activity of carotene under the experimental conditions used, but it remains to be explained how molecules, differing so obviously as do carotene and the vitamin *A* of cod-liver oil, can be interchangeable in function. Preliminary experiments by the author have indicated that a chemical relationship between carotene and vitamin *A* may exist.

P. H. P.

Vitamin *D* in Ergot of Rye. E. Mellanby, E. Surie and D. C. Harrison. (*Biochem. J.*, 1929, **23**, 710-717.)—In the course of some experiments it was observed that ergot of rye had a powerful action in promoting calcification of the bones when added to diets which, in themselves, resulted in the development of rickets. This problem has now been investigated in more detail, in order to study the properties of the calcifying substance in ergot, and to consider its relation to, or identity with, vitamin *D*. Puppies were used for the tests; comparisons were made between the animals in each litter and not between animals in different litters. Owing to its unpleasant taste, ergot can only be given to dogs in relatively small quantities. Even then, they sometimes refuse their food; consequently, in the majority of cases, the puppies given ergot did not grow as well as the other members of the family. When alcoholic and ethereal extracts of ergot replace the ergot itself the difficulties regarding the food intake are avoided. The bone conditions were diagnosed clinically and radiographically. The results of the experiments confirm the fact that ergot of rye is a powerful stimulus to calcification of bone. The substance responsible for the calcifying action is soluble in alcohol and ether, resists saponification, and has the properties, so far as these are known, of vitamin *D*. The irradiation of unground ergot grains by strong sunlight for 12 hours produces no increase, and the irradiation by the mercury-vapour lamp for half-an-hour only a slight increase in the calcifying activity of ergot, although there is abundant ergosterol present. Therefore, the covering of the ergot grains is relatively impermeable even to very abundant ultra-violet radiations. This raised a doubt as to whether the vitamin *D* was due to the direct action of sunlight on the ergosterol present in the ergot. In mushrooms, the one form of fungus tested, there was no evidence of vitamin *D*. Rye germ itself, unaffected by the ergot fungus *Claviceps purpurea*, was found to contain a small quantity of calcifying substance which can be extracted by petroleum spirit. How the ergosterol in ergot becomes activated to vitamin *D* is an unsolved problem. Although at the present time the ultra-violet irradiation of ergosterol is the only known mode of origin of vitamin *D*, it is possible that vitamin *D* can be made from ergosterol by the growing plant independently of ultra-violet radiations. Some samples of ergot contain, roughly, about one-eighth to one-quarter the calcifying activity of cod-liver oil.

P. H. P.

Organic Analysis.

Determination of Sugar in Soap and Soap Preparations. K. Braun and E. Walter. (*Chem. Ztg.*, 1929, 53, 778.)—A solution of 25 grms. of soap in 25 c.c. of water is heated on the water-bath with dilute sulphuric acid (strength not given) for 30 minutes, the fatty acids being separated and the sugar inverted simultaneously. After 12 hours the fatty acids are filtered off, washed with warm water, and the filtrate neutralised to litmus with sodium hydroxide and made up to 200 c.c. or a suitable volume. The precipitate produced from 25 c.c. of this solution and 50 c.c. of Fehling's solution in the usual way is washed free from alkali and dissolved in 50 c.c. of a solution of 50 grms. of ferric sulphate in 200 grms. of concentrated sulphuric acid, diluted to a litre, and the ferrous sulphate produced is titrated with 0.1 *N* potassium permanganate solution, 1 c.c. of which is equivalent to 0.00636 gm. of copper or (from Bertrand's tables) 0.0029 gm. of sugar. J. G.

Determination of the Total Geraniol Content of Citronella Oil. M. Van der Slik and J. Vermeulen. (*Chem. Weekblad*, 1929, 26, 482–483.)—Ten c.c. of oil are acetylated with 11.3 c.c. of 95 per cent. acetic anhydride in the presence of 1.3 grms. of dry sodium carbonate. The use of sodium carbonate avoids the difficulty and expense of procuring completely anhydrous sodium acetate where large numbers of determinations are involved, and has been shown by comparative determinations on 100 samples not to affect the results. J. G.

Determination of Mercaptans in Naphtha. P. Borgstrom and E. E. Reid. (*Ind. Eng. Chem. Anal. Edit.*, 1929, 1, 186–187.)—Ethyl, *n*- and *iso*-propyl, amyl and butyl, *sec*-butyl, pentathiol-2 and benzyl mercaptans were determined in naphtha (I.B.P. 146° C., sulphur 0.028 per cent.) by shaking a known volume with excess of silver nitrate. Two c.c. of iron alum solution and sufficient 0.05 *N* ammonium thiocyanate solution to give a deep red colour are then added, the mixture well shaken, the excess of ammonium thiocyanate removed by 0.05 *N* silver nitrate solution, and the solution finally titrated to a permanent pink colour (*cf.* Birch and Norris, *J. Chem. Soc.*, 1923, 129, 2545). The silver nitrate titration figure $\times 0.001603$ = weight of mercaptan sulphur. Alternatively, the mercaptans may be removed as silver mercaptides with silver nitrate, and the lamp method used for the determination of the residual sulphur in the liquid. This quantity is subtracted from the total sulphur found by the lamp method. The average absolute error is 0.002 per cent. for quantities of 0.05 to 0.1 per cent. of sulphur added, and is due principally to adsorption of silver nitrate by the precipitated mercaptides. Consequently, the mixture must be well shaken, 5 c.c. of alcohol being added, if necessary, before the final titration, to break any emulsion. Reduction of disulphides by zinc and glacial acetic acid decomposes the mercaptans and invalidates the titration method, but the acidified calcium chloride solution and mercury used for the removal of hydrogen sulphide and elemental sulphur, respectively, do not remove the mercaptans studied. J. G.

Reactions of Tetra-ethyl Lead. G. Edgar and G. Calingaert. (*Ind. Eng. Chem. Anal. Edit.*, 1929, 1, 221-222.)—The total lead in concentrated anti-knock preparations (which are highly poisonous) is determined by bromination of 1 c.c. at 0° C. in the presence of 25 c.c. of carbon tetrachloride. After evaporation the lead bromide is dissolved in hot ammonium acetate solution, and the lead in the filtered solution precipitated as lead chromate, or titrated while hot with a molybdate solution standardised against a solution of pure lead chloride. A fresh 0.5 per cent. solution of tannic acid is used as outside indicator, 2 drops always being added to 4 drops of solution, and a yellow colour is obtained at the end-point. For dilute solutions, 100 c.c. of petroleum are brominated with excess of a 30 per cent. solution of bromine in carbon tetrachloride, and filtered at once on a Gooch crucible, and the residue washed with petroleum spirit and dissolved in warm nitric acid. The filtered liquid is neutralised with ammonia and either of the above procedures used. The accuracy is 1 per cent. for 0.02 to 0.08 per cent. by volume of lead. Tetraethyl lead itself should be dissolved in 50 c.c. of benzene, and a known volume (15 times the weight of lead) of 0.1 N iodine solution added, the excess being titrated after vigorous shaking for 3 minutes. The reaction is $\text{Pb}(\text{C}_2\text{H}_5)_4 + \text{I}_2 = \text{Pb}(\text{C}_2\text{H}_5)_3\text{I} + \text{C}_2\text{H}_5\text{I}$, and an accuracy of 0.3 per cent. is obtainable. If di-lead hexaethyl is also present, the sp. gr. of the sample will be raised in proportion, from 1.65 to 1.95 (the value for the latter). If, however, the iodine titrations and the total lead are determined, the proportions may be calculated more accurately from the equation $\text{Pb}_2(\text{C}_2\text{H}_5)_6 + \text{I}_2 = 2\text{Pb}(\text{C}_2\text{H}_5)_3\text{I}$. Triethyl lead salts are determined in 5 c.c. of sample diluted with 20 c.c. of petroleum spirit, with an accuracy of 2 per cent., by extraction with two 20 c.c. portions of concentrated ammonia, which are then evaporated, and a solution of the residue in nitric acid is analysed for lead. J. G.

Inorganic Analysis.

Detection and Determination of Carbon Disulphide in Fluids. J. A. Pierce. (*Ind. Eng. Chem. Anal. Edit.*, 1929, 1, 227-228.)—The reagent, which is stable in the dark for a week and should remain colourless, is prepared by addition of 4 c.c. of concentrated ammonia and 3 grms. of hydroxylamine hydrochloride to 50 c.c. of 2 per cent. copper sulphate solution (Ilosvay). If the sample is an oil, it is diluted to one-half with pure chloroform, and 5 c.c. shaken gently with 2 c.c. of reagent so as to avoid an emulsion. One part of carbon disulphide in 30,000 parts of oil gives an opaque chocolate-coloured aqueous layer, which soon clears and leaves a dark, heavy slimy precipitate at the interface. The precipitate contains cuprous sulphide and an unknown substance, whilst dissolved sulphur yields a black lustrous precipitate of cuprous sulphide only, which is easily identified under the microscope. The determination is made by comparison of the colour produced with that from a standard solution of carbon disulphide in an inert oil. J. G.

Rapid Microchemical Determination of Copper and Mercury. (a) G. Spacu and J. Dick. (*Z. anal. Chem.*, 1929, 78, 241-244.) (b) G. Spacu and G. Suci. (*id.*, 244-247.)—The methods previously described for the

quantitative precipitation of the two metals (ANALYST, 1927, 494; 1929, 618) have been adapted to their microchemical determination. For practical details reference to the original papers is invited. W. R. S.

Rapid Determination of Tin in Tin Plate. K. Heuberger. (*Chem. Zeit.*, 1929, 53, 788.)—A rapid process consists in dissolving 5 grms. of cuttings in 50 c.c. of water and 75 c.c. of strong hydrochloric acid, the attack taking place in a flask closed with a valve containing bicarbonate solution. When solution, assisted by warming, is complete, the liquid is boiled for a short time and the flask cooled in running water. Twenty c.c. of hydrochloric acid and starch solution are added, and the liquid titrated at once with iodine. Three determinations require half an hour. The results obtained are always a trifle higher than those by the more tedious volatilisation method in a chlorine current, which must be due to a trace of stannic chloride escaping absorption in the receivers. For de-tinned scrap (0.1 to 0.2 per cent. tin), 10 gm. portions are taken. W. R. S.

Adsorption of Phosphoric Acid by Stannic Sulphide. R. Chandelle. (*Bull. Soc. Chim. belge*, 1929, 38, 255–258.)—Comparative determinations of phosphorus in 0.25 gm. of potassium dihydrogen phosphate in the presence and absence of 0.3 gm. of tin have shown that the error due to adsorption of phosphorus by stannic sulphide is 0.2 per cent. Care must be taken that basic tin salts, which have a greater adsorptive capacity for phosphorus, are not produced, *e.g.* by hydrolysis, $\text{SnS}_2 + 4\text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{SnO}_3 + \text{H}_2\text{O} + 2\text{H}_2\text{S}$. To this end a solution of the tin in *aqua regia* is evaporated to dryness, the residue dissolved in fuming hydrochloric acid and a few c.c. of water, and a saturated solution of hydrogen sulphide added. This also serves to precipitate the stannic sulphide which may be subsequently filtered off, the hydrogen sulphide boiled out, and the phosphate precipitated. The precipitate of magnesium pyrophosphate was found to contain 0.146 per cent. of silica. J. G.

Volumetric Determination of Manganese as Dioxide. I. M. Kolthoff and E. B. Sandell. (*Ind. Eng. Chem. Anal. Edit.*, 1929, 1, 181–185.)—The use of potassium bromate in place of the persulphate for the oxidation of manganese to manganese dioxide is recommended for the determination of this element in ores and manganese steels. A solution (50 c.c.) of sample equivalent to 20 to 150 mgrms. of manganese is made 1.0 *N* with respect to sulphuric or nitric acid, 2 grms. of potassium bromate added, and the solution boiled for 5 to 10 minutes according to the amount of iron present. The solution is filtered (twice if necessary), the precipitate of manganese dioxide washed with six 10 c.c. portions of hot water, and the iodine liberated from 2 grms. of potassium iodide, in the presence of 5 c.c. of 20 per cent. potassium fluoride solution, 75 c.c. of water and 5 c.c. of 4 *N* sulphuric acid, and titrated with 0.1 *N* sodium thiosulphate solution. If iron is absent, 4 grms. of zinc sulphate should be added to the original solution, when 1 c.c. of 0.1 *N* thiosulphate solution = 0.002801 gm. Mn. If small amounts of

iron are present, a pure ferric salt is added, so that the amounts of iron and manganese present are approximately equal, and the corresponding factor is 0.002774 gm. Mn. For small amounts of manganese in the presence of large amounts of iron, the latter must be removed by addition of a suspension of zinc oxide to a solution of the sample, but, as some manganese is also removed, the factor is 0.002834. Chromium, lead, nickel, bismuth, and chlorides do not interfere, but large amounts of phosphates, vanadium, tungstates and molybdates, introduce errors, and in the two last cases low results are obtained. J. G.

Separation of Aluminium by 8-Hydroxyquinoline. G. E. F. Lundell and H. B. Knowles. (*Research Paper No. 86, U.S. Bureau of Standards, July, 1929.*)—The precipitation of aluminium has been described by Hahn and Vieweg and by Berg (*ANALYST*, 1927, 431, 611). The authors have tested and established the reliability of the reagent for the separation of aluminium from the elements specified below. (1) *From phosphorus, arsenic, fluorine, boron*:—The slightly acid sulphate or chloride solution ($\text{Al}_2\text{O}_3 < 0.1$ gm. per 100 c.c.) is treated with an excess of reagent, followed by dilute ammonia till alkaline, and then with 5 c.c. of strong ammonia. The liquid is digested at 60° to 70° C. till the precipitate becomes dense and crystalline. After cooling (preferably in ice-water), the precipitate is collected on paper of close texture and washed with dilute ammonia (1:40) containing 25 c.c. of reagent, neutralised with ammonia, per litre. (The reagent is made by the trituration of 2.5 grms. of the base with 5 c.c. of glacial acetic acid, pouring into 100 c.c. of water at 60° C., and filtering after cooling; 1 c.c. precipitates 2.9 mgrms. of alumina.) The precipitate and paper are heated with nitric and sulphuric acids; after destruction of the paper the alumina is precipitated with ammonia, as usual; a correction for silica is applied, if necessary. (2) *From vanadium, tantalum, niobium, titanium, molybdenum*:—In the method described under (1), 10 to 15 c.c. of 3 per cent. hydrogen peroxide are added before the reagent; otherwise the technique is the same. (3) *From uranium*:—The method outlined under (1) is applied, except that ammonium carbonate is used; the faintly acid solution is neutralised with a saturated ammonium carbonate solution, of which an excess of 25 c.c. per 100 c.c. of assay solution is afterwards added. In heating to 50° C. excessive effervescence should be avoided. (4) *From beryllium* (see *ANALYST*, 1928, 508; 1929, 434):—Double precipitations are hardly required. Rapid, if slightly low, results were obtained with ingot iron and ferrovanadium by dissolving in acid, neutralising with alkali, and pouring slowly into caustic soda solution. An aliquot part of the filtrate was treated as under (1) in the case of the iron, and (2) the ferrovanadium. The reagent will also detect aluminium in phosphoric acid and alkali phosphate (when ammonia gives no precipitate) when added to the ammoniacal solution. W. R. S.

Detection and Determination of Sulphur Dioxide. S. Rothenfusser. (*Z. Unters. Lebensm.*, 1929, 58, 98–109.)—The sample is heated in a 500 c.c. flask with 300 c.c. of water, 10 c.c. in excess of 25 per cent. phosphoric acid and about

0.5 gram. of pumice powder (and 5 c.c. of paraffin in the case of meats) attached to a vertical condenser, and the distillate is collected in a mixture of 5 c.c. of a filtered 5 per cent. solution of benzidine in 96 per cent. alcohol 5 c.c. of 30 per cent. acetic acid, and 5 c.c. of 3 per cent. hydrogen peroxide are added. The sulphur dioxide is oxidised to sulphuric acid and forms benzidine sulphate which is insoluble in acetic acid. The precipitate is filtered in the cold, washed three times with 5 c.c. of water, dried for 30 minutes at 105° C. and weighed. The factor 0.234 gives the weight of sulphur dioxide, or the precipitate may be titrated with 0.1 N sodium hydroxide solution, or decomposed with hot hydrochloric acid, and precipitated with barium chloride. The advantages claimed are quick removal of sulphur dioxide in the presence of the pumice, the high molecular weight of the benzidine compound, and the fact that it is non-volatile and forms characteristic crystals which may be used for identification in qualitative tests. Carbon dioxide is not required, and the solubility of the precipitate is unaffected by the presence of other volatile substances, including alcohol, in the amounts likely to occur.

J. G.

Platinised Silica Gels as Catalysts for the Oxidation of Sulphur Dioxide. H. N. Holmes, J. Ramsay and A. L. Elder. (*Ind. Eng. Chem.*, 1929, 21, 850-853.)—At temperatures about 395° C., that is, slightly below those required for the maximum conversion of sulphur dioxide into sulphur trioxide, platinum deposited on chalky (porous) silica gel is more efficient as a catalyst than platinum on glassy silica gel. At 440° to 450° C., the temperature for maximum conversion, there is but little difference in the efficiency of the two gels as supporters for the platinum catalyst. Under similar conditions, platinum deposited on either of the gels is more efficient than is platinum deposited on asbestos.

W. P. S.

Determination of Silica in the Presence of Fluorspar. W. T. Schrenk and W. H. Ode. (*Ind. Eng. Chem. Anal. Edit.*, 1929, 1, 201-202.)—The method of Berzelius is accurate but tedious, and the only satisfactory alternative is that suggested in which 0.5 gram. of powdered sample is digested with 15 c.c. of 20 per cent. perchloric acid saturated at 50° C. with boric acid. After the acid fumes have been evolved for 5 minutes the mixture is diluted, the evaporation repeated, and 60 c.c. of water added. The filtered off precipitate is washed free from calcium salts with hot water, ashed in the presence of a little sulphuric acid, and ignited till constant in weight. Silica is finally removed from the residue in the usual way, and the loss in weight determined. The error is ± 0.05 per cent. for 0.06 gram. of silica in 0.5 gram. of sample. Omission of the boric acid leads to low results.

J. G.

Physical Methods, Apparatus, etc.

Application of X-rays in the Classification of Fibrous Silicate Minerals commonly termed Asbestos. H. V. Anderson and G. L. Clark. (*Ind. Eng. Chem.*, 1929, 21, 924-933.)—Thirty different specimens of fibrous minerals from different parts of the world were examined, and illustrations of the diffraction

patterns for the natural fibres, and the same after digestion with hydrochloric acid and after ignition are given. A table of the properties of the minerals includes a description of the appearance of the natural fibre; the calculated identity period in Ångström units, along the fibre axis, from X-ray diffraction data; the percentage loss in weight after acid treatment; the percentage loss in weight after heating; the physical properties after heating, etc. W. P. S.

Reviews.

REPORTS OF THE PROGRESS OF APPLIED CHEMISTRY. Vol. XIII for 1928. Issued by the Society of Chemical Industry. Pp. 741. Price to members, 7s. 6d.; to non-members, 12s. 6d.

These annual reports have firmly established themselves in the favour of chemists in all branches of the scientific industries, and the present volume, equal in size to its immediate predecessors, will enhance their reputation.

There are 25 separate sections, that on "Explosives" dealing with the two years 1927-28. Each one of these sections is a mine of information, and an adequate bibliography of the important discoveries, observations and points of progress in the particular subject with which it deals.

Under "General, Plant and Machinery" (A. J. V. Underwood), attention is directed to the larger amounts of capital now being employed in Germany in the manufacture of nitrogenous fertilisers and the liquefaction of coal, and it is stated that the chemical industry is in most countries—including this country—increasing production and showing larger profits. In Great Britain, however, there is no improvement in the staple industries of coal, steel and cotton. The rapid progress in nitrogen fixation (interestingly reviewed also in the section on "Acids, Alkalis, etc.") will mean more severe competition for the Chilean nitrate industry.

A new adsorbent described consists of an inert siliceous material impregnated with calcium chloride, the mixture having a large capacity for taking up water, which is removable on heating. Various new types of viscosimeters are noted, as also a sampling device for solid materials, by which they can be automatically quartered. Another automatic apparatus determines the small amounts of sulphur dioxide in the air, and this should be of use in connection with work on atmospheric pollution.

The section on "Fuels" (H. J. Hodsmen) deals with numerous topics, including domestic heating, pulverised coal, smokeless semi-coke and coke, and with the origin and chemistry of coal. Some of these subjects are also referred to in the next section ("Gas, Carbonisation, Tar and Tar Products," by H. Hollings).

A full review of the present position of artificial silk is given in the section on "Fibres, Textiles, etc.," (J. C. Withers), while the dyeing of this artificial fibre and of the older natural fibres is considered in "Bleaching, Dyeing, etc.," by L. G. Lawrie. A short sub-section on analytical methods appears in the former section.

Papers on the identification of artificial silk by means of ultra-violet rays are referred to in the same article. The results of enquiries into the alleged poisonous properties of lead tetraethyl, when used as "dope" in petrol, are discussed in the section on "Acids, Alkalis, etc.," while there are in the volume also articles on stainless steels, corrosion and protection of metals and alloys, chromium plating and the electro-chemical industry generally.

In Dr. Hilditch's section on "Oils, Fats and Waxes," some German figures are given showing that the consumption of margarine in Great Britain exceeds that of butter, but the reviewer thinks the statistics on this point require verification. Vitamin-containing margarines being now on the market, it would seem desirable to call attention to the warning given in another section ("Foods") of the possible danger from foods artificially vitaminised, owing to over-dosage. Important work is described in connection with the constitution of fats; rancidity, the detection of hardened fats, and the differentiation of liver oils from other fish oils. The chemistry of the vitamins is also dealt with in the sections on "Fine Chemicals, Medicinal Substances, etc." (W. H. Linnell) and on "Foods," and these articles reveal the ever-increasing complexity of the subject. Reference is also made in the section on "Foods" (Aumonier and King) to papers on the "fishiness" of certain dairy products, which property has been shown to be due to the presence of appreciable traces of copper in these foods. No reference, however, is made, in this connection, to the possibility of a "fishy" taste being communicated to foods by reason of the presence of fish meal in the diet of dairy animals.

A suggestion for a method of differentiating between artificial cream and the real article is based on the different colloidal condition of the proteins. The writers on "Foods" (p. 583) say, on the subject of preservatives in foods: "There is some evidence that the public are not altogether satisfied with the results of two years' experience of the Preservatives Regulations. . . . An epidemic of paratyphoid has been commented on in this connection." If the cogency of the evidence against the Regulations is to be assessed on the last sentence quoted, it may be said that the critics, spoken of by the writers of this section, are ill-informed. No preservative known, used in the amounts possible in foods, would have any effect on such infected food; and, had there been no regulations restricting the use of preservatives, the infected food would still have been toxic.

The methods in use for the rapid determination of sulphur dioxide in foodstuffs, recommended by a Committee of chemists engaged in the food manufacturing industries, and published in *THE ANALYST*, receive favourable mention, and those who have experience of them will agree that these methods are reliable and accurate.

The interesting article on "Soils and Fertilisers," by E. M. Crowther, should be read by all agricultural chemists.

The typographical errors in the volume are remarkably few, and those noticed are fairly obvious. There are adequate indexes of authors and subjects, and the book is throughout a worthy production.

ARNOLD R. TANKARD.

THE ANALYSIS OF DRUGS AND CHEMICALS. By NORMAN EVERS, B.Sc., F.I.C., and G. D. ELSDON, B.Sc., F.I.C. Pp. x+372. 8vo. London: Charles Griffin & Co., Ltd. 1929. Price 25s. net.

In their introduction the authors rightly call attention to the fact that one of them is a pharmaceutical works chemist, and the other a public analyst. From such a combination of experienced workers, it is reasonable to expect something exceptional in the way of a book on the analysis of drugs and chemicals, and so far as one can tell from perusal of its contents, such an expectation is not likely to be disappointed. There is an admirable introduction on laboratory methods and a useful appendix of 25 pages of tables.

The subject-matter proper is divided into six parts—inorganic drugs and chemicals; organic chemicals; crude drugs; galenicals; fixed oils, fats and waxes; and essential oils. Where general methods of examination are feasible, they are described in the introduction to each part, and under each material dealt with, practically everything the analyst requires to know for its examination is given with a brevity and clarity that are refreshing. The few slips noticed are not such as to detract from the value of the book as a trustworthy analytical guide; for example, it seems a pity in a chemical text book to apply the term "arsenobenzene" to what is a derivative of this substance, when the name "arsphenamine" is available, and is in common use. The fact that "arsenobenzene" is so used in the Therapeutic Substances Act does not justify chemists in perpetuating this official misuse of the term. Similarly, there are advantages in adhering to the usual British plan of writing *iso*Butyl- and *iso*Amyl- instead of *Isobutyl*- and *Isoamyl* (p. 128). Apart from trifling points of this kind, the book has been carefully prepared, and is in every way a creditable production on which the authors are to be congratulated.

T. A. HENRY.

PRACTICAL PLANT BIOCHEMISTRY. By MURIEL WHELDAL ONSLOW, M.A., Lecturer in Plant Biochemistry, University of Cambridge. Third edition. Pp. iv+206. Cambridge: University Press. 1929. Price 12s. 6d. net.

The first edition of Mrs. Onslow's *Practical Plant Biochemistry* appeared in 1920, the second one in 1923, and there is no doubt that there was a demand for the third edition. The book has become indispensable to every student and teacher of plant chemistry. In many ways the present edition differs very little from the preceding one, and, in glancing through, one gets the impression of a reprint. Even as regards points about which our views have undergone fundamental changes, subject-matter, and formulae, such as that for phytol (p. 39), have not been revised. On the other hand, all sugar formulae have been changed from the five ring to the six ring structure, which is perhaps too confidently accepted, since these formulae, although fashionable at present, are still open to satisfactory confirmation.

In spite of these minor points, perhaps of exaggerated importance in the eyes of the reviewer, Mrs. Onslow's book remains an invaluable chart to all those who explore the field of Plant Chemistry.

M. NIERENSTEIN.

AN INTRODUCTION TO THE CHEMISTRY OF PLANT PRODUCTS. Vol. II: METABOLIC PROCESSES. By P. HAAS, D.Sc., Ph.D., and T. G. HILL, D.Sc., A.R.C.S. Second edition. Pp. viii+220. London: Longmans, Green & Co. Price 10s. 6d. net.

It must require a certain amount of courage on the part of an author to write a book on the metabolic processes of plants, if only for the reason that so little is known with certainty about these processes. A subject in this condition is apt to accumulate about itself a large number of contradictory and inconclusive observations, and the first duty of the writer of a text book is that of the selective critic, the second that of presenting the selected data as briefly and clearly as possible, so that his readers may get a trustworthy idea of the present state of the particular problem.

Messrs. Haas and Hill have divided their material into six chapters, the first dealing with the living plant from germination to reproduction, and the remaining five with growth, respiration and the synthesis of carbohydrates, fats and proteins, the five great problems with which plant physiologists are concerned. The treatment of each is admirably adapted to distinguish established fact from plausible speculation, and to stimulate interest in, and further work on, these problems.

The reviewer, as a chemist, has no right to complain of biological terminology, but he does venture to suggest that it must be discouraging to a young chemist beginning to take an interest in phytochemical problems to meet with such a paragraph as the following on the third page of this book:

"Circumnutative and other autonomous movements may be explained by such conceptions as rectipetality and associated engrams; whilst in explanation of tropisms various mechanistic hypotheses have been formulated, some chemical, the hormone theory of gravitational stimulus of roots, for instance; others physical, the statolith theory, for example."

It is only fair to add that this is practically the sole lapse into technical obscurity, but it is noticeable because it comes so early in the book. The first volume, which has already been noticed in *THE ANALYST* (1928, 53, 681), forms with this companion volume an admirable introduction to the study of plant products, which will be no less popular with students and teachers than the previous editions.

T. A. HENRY.

A HANDBOOK OF CLINICAL CHEMICAL PATHOLOGY. By FRANK SCOTT FOWWEATHER, M.D., M.Sc., D.P.H., F.I.C. Pp. x+216. London: J. A. Churchill. 1929. Price 8s. 6d. net.

The rapid growth of Chemical Pathology has raised it to a position of great importance as an aid to clinical diagnosis, treatment and prognosis in all branches of medicine. In view of the ever-increasing additions to the literature, a book dealing with the interpretation of analyses, rather than technical details, should be welcomed by both medical practitioner and analyst. Dr. Fowweather may be congratulated on producing a work of this character.

In the foreword by Lord Moynihan, and in the preface, it is clearly indicated that the book is in no way intended to be a practical manual for chemists, and no attempt is made to describe in detail the actual methods of chemical analysis. The author has, in the main, confined himself to the consideration of the theory of chemical processes in disease; the indications for, and clinical procedure involved in carrying out the required tests (including the taking and preservation of specimens); and the interpretation of the results of chemical analysis.

The subject-matter is well arranged and covers the field of chemical pathology with remarkable completeness. The chemical investigation of the functions of the alimentary tract and of the organs concerned in the processes of digestion and excretion receives full treatment. The author's statement on page 76 to the effect that, "Personally, I have rarely got a convincing biphasic reaction (*re* Van den Bergh Test) even where it is most to be expected," will occasion some surprise. In the hands of others the frequent occurrence of this type of reaction constitutes one of the serious limitations of the test as a clinical aid.

The author raises an interesting point with regard to the estimation of fat in faeces. It is his opinion that, since the reaction of the faeces is often alkaline, a certain amount of hydrolysis of fat must result from the usual practice of drying the faeces at a high temperature in the preparatory stages of analysis. To obviate this difficulty he suggests that the differential fatty content of the fresh stool should first be estimated, and that the values so determined should subsequently be expressed as percentages of the total dry matter as estimated from the desiccation of an equal portion of the fresh material. The use of a vacuum-desiccator at room temperature in the preliminary steps of the preparation of a dried specimen of faeces would exclude the possibility of hydrolysis, and is certain to commend itself to chemists as a cleaner and better way out of the difficulty than the method advocated.

The chapter on "Tests on the Cerebro-Spinal Fluid" would benefit from the addition of a table embodying a summary of the comparative findings in the various diseases of the Central Nervous System. The concise theoretical treatment of such subjects as "The Acid-Base Equilibrium of the Blood," "Ossification; Calcification; and Calculus Formation," "The Changes in the Cholesterol, Phosphorus, and Calcium of the Blood," and "Vitamins and Deficiency Diseases," considerably enhance the value of the volume as a handbook of reference.

The author is clearly an enthusiast, for, having led the reader skilfully through the range of chemical pathology from P_{H} values to vitamins, he finishes on a lofty note by quoting comic verse—a method of expression which is, perhaps regrettably, unusual in works of this character.

The book is well indexed, but it seems a pity that the principal references to the various topics are not indicated in heavy print.

In my opinion the work admirably fulfils its mission, and I am glad to add it to my bookshelves.

W. HURST BROWN.

A. B. L. 75

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